Volume 1 *October, 1931* *Number 4*

PHYSICS

NATURAL OBSERVATION LIMIT OF RADIOMETRIC MEASUREMENTS

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(Received July 20, 1931)

Abstract

The sensitivities of thermocouples, radiomicrometers, bolometers, expansiometers and radiometers are compared by determining the minimum amount of energy that can be detected by a single observation. The instruments are considered to be critically damped and the accuracy of the measurements to be limited by the Brownian motion fluctuations of the measuring device. A detectable deflection is arbitrarily taken as four times as large as the Brownian motion fluctuations. The theoretical considerations are included for their generality or for their direct bearing on the practical design and use of the instruments. A thermocouple with a galvanometer or a radiomicrometer is the most sensitive of the measuring instruments considered. By a single observation with a galvanometer of one sec. period, 3×10^{-11} gm·cal./sec. falling on a thermocouple receiver 1 mm² should be detected. A complete theory of the vacuum bolometer is presented. The ideal sensitivity of a vacuum bolometer is approximately the same as for a thermocouple but practical difficulties make the bolometer less sensitive. The vacuum tube is less sensitive than a galvanometer for use with a thermocouple or bolometer. A thin bimetallic receiver would not be as sensitive as a thermocouple for making accurate radiometric measurements. A vacuum thermocouple is about 20 times more sensitive than a radiometer mostly because the gas pressure that is needed for the action of the radiometer only allows the receiver to be heated about 1/10th as high as a vacuum thermocouple receiver. The sensitivity of a critically damped galvanometer or radiometer, limited by the Brownian motion, is proportional to the square root of the period.

THE accuracy of present day radiometric measurements is determined by the natural observation limit imposed by the random Brownian motion fluctuations of the measuring system. Since thermocouples, radiomicrometers, bolometers, extensiometers, and radiometers can be used for the same kind of radiometric measurements, it is important to know which instrument is the most sensitive and the magnitude of the smallest amount of radiant energy that can be detected by any of them. The desirability that the instruments be critically damped together with the inherent fluctuations of the readings due to Brownian motion give a definite measure by which to compare the instruments and determine their ultimate sensitivities.

The sensitivities of different instruments as determined by the magnitude of their deflections under identical conditions is interesting and useful but for precise measurements the information is not complete; it is equally important to know the accuracy with which the scale can be read. This is true

particularly since the Brownian motion fluctuations can be made large. The readings can be magnified by a great scale distance or a thermal relay so that the Brownian motions actually limit the sensitivities of the instruments.

The effect of Brownian motion is used in a very general sense. The measuring device can be considered as having one degree of freedom and therefore by the equipartition law as having an average potential energy of $\frac{1}{2}kT$ and an average kinetic energy of $\frac{1}{2}kT$. Since readings of position only are made, the $\frac{1}{2}kT$ of potential energy is all that needs to be considered. The fluctuation can be considered as due to the random bombardment of the gas molecules, motions of the molecules in the suspension, or surges of electrons through the galvanometer. The Brownian motion can be considered as defining the temperature of the moving system. The fluctuation would not be removed by operating a galvanometer in a perfect vacuum; the character of the fluctuations might be changed but the magnitude would remain the same.

The fluctuations of the zero position of a galvanometer have been observed for a long time but they were not considered as inherent in the galvanometer; that is, the inherent fluctuations due to Brownian motion were not estimated as being nearly so large. Moll and Burger[1] in 1925 published some photographs which showed incidentally the fluctuations of a galvanometer as recorded on a moving film. The fluctuations were attributed to microseismic vibrations. In 1926, G. Ising[2] explained the fluctuations just described as of the right order to be expected from the Brownian motion of the galvanometer coil. Later Zernike[3] showed that the same result was obtained by only considering surges of electrons in the galvanometer circuit with an average energy of $\frac{1}{2}kT$.

From efficiency considerations, one may expect that the natural limit of sensitivity for these different types of instruments should be about the same; however, in every case, the efficiencies are so extremely small that a factor of 10 or even 100 may separate the instruments. Also, the present instruments may possibly be greatly improved by discovering better thermoelectric elements and a better material for bolometers. For an ideal vacuum thermocouple, the efficiency of the transfer of the radiant energy by absorption into electrical energy was confirmed experimentally to be about 10^{-8} percent for the small but measurable quantity of radiant energy of 10^{-11} gm·cal./sec. striking the thermocouple receiver of 1 mm^2 area. It was also determined experimentally that the vanes of a radiometer are only heated about 1/8 as much as the receivers of a vacuum thermocouple because they are cooled by the gas which is essential for the radiometric pressure. Radiometers are therefore handicapped because the sensitivities of the instruments considered are proportional to the heating of their receivers.

The motion of the measuring device (a galvanometer for a thermocouple, radiomicrometer, or bolometer) is defined by the equation

$$I\ddot{\theta} + D\dot{\theta} + K\theta = F \tag{1}$$

[1] Moll and Burger, Phil. Mag. **50**, 830 (1925).
[2] G. Ising, Phil. Mag. **11**, 827 (1926).
[3] F. Zernike, Zeits. f. Physik **40**, 628 (1926).

where I is the moment of inertia of the moving system, θ the angular deflection, D the damping constant, K the torsion constant of the suspension, and F the torque produced by the energy to be measured.

The desirability that the deflections be critically damped imposes the condition

$$D = 2(IK)^{1/2}. \tag{2}$$

The time, t_0, for a deflection is approximately

$$t_0 = 2\pi(I/K)^{1/2}. \tag{3}$$

The energy of the moving system is

$$\epsilon = \tfrac{1}{2}K\theta^2 + \tfrac{1}{2}I\dot{\theta}^2. \tag{4}$$

Using Boltzmann statistics, the average energy of the fluctuations of the moving system defined by Eq. (4) is kT, therefore the average potential energy is $\frac{1}{2}kT$.

Ising arbitrarily assumed that a measurable quantity should cause a deflection of four times the displacement due to $\frac{1}{2}kT$ of potential energy. The probability that the deflection will lie at any instant in the range θ to $\theta+d\theta$ is

$$\text{Probability} = \left(\frac{K}{2\pi kT}\right)^{1/2} e^{-K\theta^2/2kT}d\theta. \tag{5}$$

Therefore, the probability of the measuring system being in the zero position is $e(e=2.7)$ times more than with a displacement due to $\frac{1}{2}kT$ of potential energy and $e^4(e^4=55)$ times better than with a displacement due to $2kT$ of potential energy.

For a galvanometer, a solution to Eq. (1) is

$$\theta = \frac{HNlbi}{K} = \frac{Gi}{K}, \tag{6}$$

where i is the current that flows in through the galvanometer and G is the dynamic or displacement constant of the galvanometer. H is the magnetic field strength, N the number of turns in the galvanometer coil and lb is the area of one turn. If the air resistance is neglected, Eq. (2) becomes,

$$D = 2(IK)^{1/2} = G^2/R_c, \tag{7}$$

where R_c is the total critical damping resistance. If $(\delta\theta)_{\text{min.}}$ is the minimum displacement that can be measured, the minimum current detectable according to Eq. (6) is

$$(\delta i)_{\text{min.}} = (K/G)(\delta\theta)_{\text{min.}}. \tag{8}$$

The displacement due to the average Brownian motion fluctuations is related thus:

$$\tfrac{1}{2}K\overline{d\theta^2} = \tfrac{1}{2}kT. \tag{9}$$

If

$$(\delta\theta)_{\text{min.}} = 4(d\theta^2)^{1/2} \tag{10}$$

as arbitrarily assumed by Ising, and if K and G are eliminated from Eq. (8) by substituting Eq. (3) and (7), the minimum current thus detectable with a critically damped galvanometer at room temperature is

$$(\delta i)_{\text{min.}} = 4.48 \times 10^{-10} \frac{1}{(t_0 R_c)^{1/2}} \text{ amps.} \tag{11}$$

and the minimum voltage detectable is

$$(\delta V)_{\text{min.}} = 4.48 \times 10^{-10} (R_c/t_0)^{1/2} \text{ volts.} \tag{12}$$

These formulas, as derived by Ising, are remarkable for their complete generality. No reference is made to the actual construction of the galvanometer, the galvanometer may well be built very rugged and good conducting leads may be used for connecting the coil to the galvanometer terminals and a thermorelay amplifier can be used to give deflections as large as is desired.

It is to be noticed that the true sensitivity of a critically damped galvanometer as limited by Brownian motion is proportional to the square root of the period. This result will be found to be equally true for expansiometers and radiometers. If the effect of Brownian motion and the desirability for the instruments to be critically damped are neglected, the sensitivities are proportional to the square of the period as determined by Eqs. (3) and (8). This difference accounts for the fact that the comparative sensitivity of many instruments is greatly overestimated. For accurate measurements, it is important that the instruments be critically damped or very slightly under damped. If an instrument is over damped, the final deflection is approached slowly and a longer time than t_0 is required for making the measurement. Greater sensitivity and accuracy could be gained by increasing the period of the instrument, t_0, and making it critically damped. If the instrument is under damped, a longer time than t_0 is required for making the measurement. Greater sensitivity could be gained by increasing the magnetic field for a galvanometer or the distance between the receivers for a radiometer. The sensitivity could be further increased by increasing the period to the time that was required for making measurements with the undamped instrument. Thus the instruments should be critically damped not only because the measurements can be made more accurately and conveniently but also because the sensitivity of the instruments is increased.

In the following the minimum amount of radiant energy detectable by a single observation as limited by Brownian motion is determined for the different instruments. The instruments are considered as *critically damped* and as far as possible the period will be taken as one second. An observable deflection will arbitrarily be taken as four times the deflection that corresponds to the average Brownian motion of $\frac{1}{2}kT$. A scheme for decreasing the effect of Brownian motion by averaging the fluctuations over a longer time than t_0 can be applied equally well to any of the instruments.

An instrument capable of measuring the smallest of radiant energy will will not necessarily be the most sensitive as measured by comparing the size of

the deflections. It may mean that smaller deflections can be read with a higher accuracy.

1. Thermocouple with Separate Galvanometer

Since the deflections are to be read so accurately that the Brownian motion fluctuations limit the measurements, the use of a thermocouple with a separate galvanometer is convenient for the galvanometer can more easily be kept free from mechanical vibrations and a thermal relay can be easily used for amplifying the deflections.

The cold junctions of the thermocouple shown in Fig. 1 are insulated from each other and are considered as maintained at the temperature T. In this type of construction, the Joule heat would increase the sensitivity; however, it can be shown that the Joule heat for measurements of the order of the Brownian motion is extremely small so that it can be neglected.

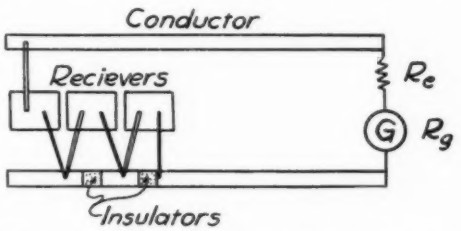

Fig. 1. Thermocouple with n junctions in series.

For the equilibrium state, the heat gained by the thermocouple (radiant heat) can be equated to the heat lost (radiation from the receiver, conduction through the leads, and Peltier heat) thus:

$$nIA(1 - r_v) = n\{4\sigma T^3 A(e_1 + e_2) + \lambda_1 x_1 + \lambda_2 x_2\}\Delta T + nJP_T T/4.18 \text{ gm}\cdot\text{cal./sec.} \tag{13}$$

where I is the intensity of radiation falling onto the receivers each of area A, r_v the reflectivity of the front surface of the receiver for the light to be measured, J the current in the circuit, R_t the resistance of the thermocouple, θ the Stefan-Boltzmann constant of total radiation, e_1 and e_2 the emissivities of the front and back surfaces of the receivers, λ_1 and λ_2 the thermal conductivities of the thermoelectric wires, x_1 and x_2 the cross-sectional areas of the wires divided by the lengths between the hot and cold junctions, ΔT the temperature of the hot junctions above the cold junctions, and P_T the thermoelectric power of the wires at the absolute temperature T. The emissivity of the thermoelectric wires has been neglected because practically the wires can be made very small and short and their emissivity corresponding to their temperature is very low. The Thompson heat is very small and may be neglected.

The current which flows through a critically damped galvanometer is then

$$J = \frac{nP_T\Delta T}{R_c}$$

$$= \frac{P_T nIA(1 - r_v)}{\{4\sigma T^3 A(e_1+e_2)+\lambda_1 x_1+\lambda_2 x_2\}\left\{R_G+R_e+\frac{n}{k_1x_1}+\frac{n}{k_2x_2}\right\}+\frac{nP_T{}^2T}{4.18}} \text{ amps.} \tag{14}$$

where K_1 and k_2 are the electrical conductivities of the thermoelectric wires.

The amount of radiant energy, ϵ, that can be detected is found by combining Eq. (11) with Eq. (13) thus:

$$\epsilon = nIA$$

$$= \frac{4.48\times10^{-10}\left\{(R_G+R_e+\frac{n}{k_1x_1}+\frac{n}{k_2x_2})\left[4\sigma T^3A(e_1+e_2)+\lambda_1x_1+\lambda_2x_2\right]+\frac{nP_T{}^2T}{4.18}\right\}}{\left[t_0\left(R_G+R_e+\frac{n}{k_1x_1}+\frac{n}{k_2x_2}\right)\right]^{1/2}P_T(1-r_v)} \tag{15}$$

$$\frac{\text{gm}\cdot\text{cal.}}{\text{sec.}}.$$

The minimum value of ϵ as a function of the two variables x_1 and x_2 is found by solving simultaneously

$$\frac{\partial\epsilon}{\partial x_1} = \frac{\partial\epsilon}{\partial x_2} = 0. \tag{16}$$

These equations are satisfied by

$$\lambda_1 k_1 x_1{}^2 = \lambda_2 k_2 x_2{}^2. \tag{17}$$

Since the electrical resistance of the wires is most easily determined, equation (17) can be expressed in terms of the resistance of the two kinds of wires thus

$$R_1/R_2 = \lambda_1 k_2/\lambda_2 k_1, \tag{18}$$

where $R_1+R_2=R_t$. Therefore, if the Wiedemann-Franz law holds[4] for the thermoelectric elements used, Eq. (18) shows that the resistance of the two wires should be the same.

If the Wiedemann-Franz law holds,

$$\frac{2n}{k_1x_1} = \frac{2n}{k_2x_2} = R_t \tag{19}$$

and Eq. (15) becomes

$$\epsilon_{\min.} = \frac{4.48\times10^{-10}\left\{(R_G+R_e+R_t)\left[4\sigma T^3A(e_1+e_2)+\frac{4nB}{R_t}\right]+\frac{nP_T{}^2T}{4.18}\right\}}{[t_0(R_G+R_e+R_t)]^{1/2}P_T(1-r_v)} \tag{20}$$

$$\frac{\text{gm}\cdot\text{cal.}}{\text{sec.}}.$$

[4] A. Sommerfeld, Zeits. f. Physik **27**, 27 (1930).

In Fig. 2 on curves a, b, c, and d is plotted $\epsilon_{\min.}$ as a function of the galvanometer resistance as given by Eq. (20). R_c is considered as zero. Two sizes of receivers are considered, 0.5 mm² and 1 mm². The thermocouple is considered as operated at $T=293°C$ with a thermocouple power of 120 μv/°C. The value of B is 1.74×10^{-6} cal·ohm/sec. and σ is 1.37×10^{-12}. The relations $R_g=R_t=(1/2)R_c$ and $2R_g=R_t=(2/3)R_c$ were taken because they approximate the conditions for critical damping found in some commercial galvanometers. The period of the galvanometer was taken for ease in comparison as 1 sec. The values $r_g=0$ and $e_1+e_2=1$ were taken for they were found approximately correct for most work.

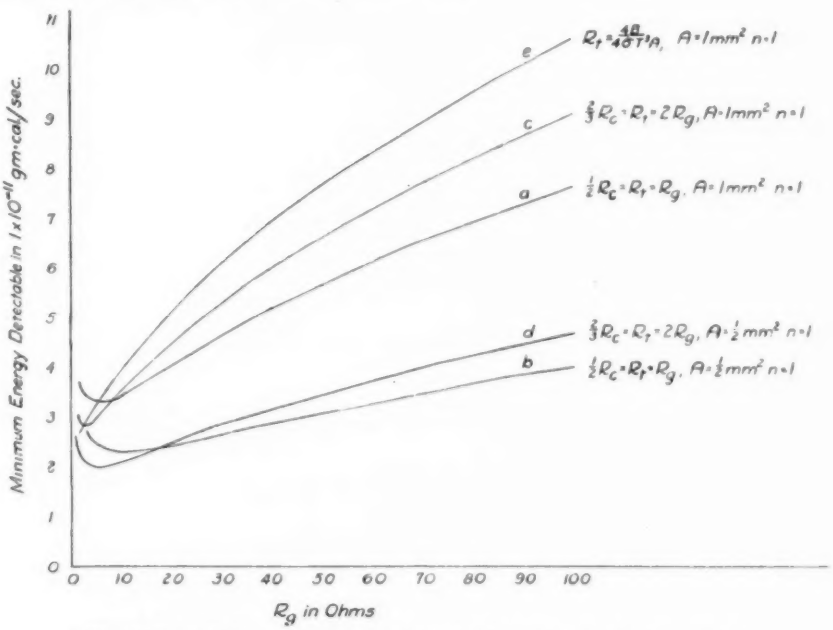

Fig. 2. Sensitivity of thermocouple and galvanometer of 1 sec. period.

The maximum power transfer occurs in a galvanometer and battery circuit when the resistance of the galvanometer is equal to the internal resistance of the battery but such a condition is usually not the most desirable for a thermocouple and galvanometer combination either for the maximum deflection of the galvanometer or for the detection of a minimum amount of radiant energy.

If the magnetic field of the galvanometers available can not be changed to bring about critical damping, the ratio of R_c to R_g will be given by the manufacturer. Therefore R_c can be set equal to sR_t in Eq. (11) and the resulting equation can be differentiated with respect to R_t which gives

$$R_t=\frac{4nB+nP_T^2T/s\times4.18}{4\sigma T^3A(e_1+e_2)}\text{ ohms.} \tag{21}$$

The minimum of curves a, b, c, and d then correspond to the R_t and s given

by Eq. (21) when substituted into Eq. (20). If the Peltier effect is neglected,* Eq. (21) expresses physically that the thermocouple receiver should lose the same amount of heat by radiation as by conduction through the thermoelectric wires.

If A' is the smallest area onto which the radiant energy to be measured can be conveniently concentrated, and a certain galvanometer of resistance R_g is to be used which requires an external critically damping resistance R_t, the optimum number of junctions to use can be found by differentiating equation (20) with respect to n after replacing A by A'/n. This gives

$$n^2 = \frac{46T^3A'(e_1 + e_2)}{\dfrac{4B}{R_t} + \dfrac{P_T^2T}{(R_t + R_6)\cdot 418}}. \tag{22}$$

It may be observed that Eqs. (21) and (22) are identical and therefore have the same physical meaning.

If the galvanometer can be made critically damped by changing the resistance of the magnetic field, the optimum resistance for the thermocouple is obtained by differentiating Eq. (20) with respect to R_t, this gives

$$R_t = \frac{nB + [n^2B^2 + 8R_GnB\sigma T^3A(e_1 + e_2)]^{1/2}}{2\sigma T^3A(e_1 + e_2)} \text{ ohms}. \tag{23}$$

if the effect of the Peltier heat is neglected. Curve e in Fig. 2 was obtained by substituting Eq. (23) into Eq. (20) for a single receiver thermocouple of 1

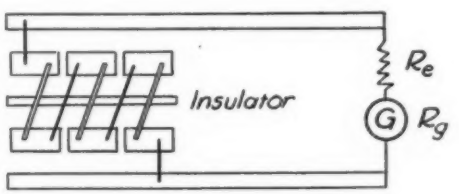

Fig. 3. Thermocouple with n junctions in series and n compensating junctions.

mm² area. The best choice for R_t and n can be found best by solving Eq. (21) for different integral values of n and then finding the corresponding $\epsilon_{\min.}$ by Eq. (20). This procedure is best for Eqs. (21) and (20) can not in general be solved exactly since n must be an integer.

The purpose of the curves in Fig. 2 is to help one in the selection of the best thermocouple design and to show how the absolute magnitude of the sensitivity $\epsilon_{\min.}$ is affected by various conditions.

A compensated thermocouple as shown in Fig. 3 has the advantage over the noncompensated type and is therefore very often used for the drift and unsteadiness of the galvanometer is greatly reduced. However, unless all of the junctions can be utilized by alternately illuminating the two sets, the

* For thermocouples of practical design, the Peltier effect gives a correction of usually less than 10 percent.

set of compensating junctions represent an external resistance and therefore a loss in the galvanometer circuit. The Joule heat is completely balanced but the Peltier heat is twice as big as for the thermocouple shown in Fig. 3. The insulating support between the two sets of junction as shown in Fig. 3 not only increases the ruggedness and makes a repair more possible but it does not decrease the sensitivity of the thermocouple.[5]

The minimum amount of radiant energy detectable by only illuminating one set of junctions is found similarly as Eq. (20) to be

$$\epsilon_{\min.} = \frac{4.48\times10^{-10}\left\{(R_G+R_e+R_t)\left[4\sigma T^3 A(\epsilon_1+\epsilon_2)+\frac{8nB}{R_t}\right]+\frac{2nP_T^2T}{4.18}\right\}}{[t_0(R_G+R_e+R_t)]^{1/2}P_T(1-r_v)} \quad \frac{\text{gm}\cdot\text{cal.}}{\text{sec.}}. \tag{24}$$

The analysis for optimum conditions is similar for the two types of thermocouple construction.

For a compensated thermocouple, Eqs. (21) and (22) become

$$R_t = \frac{8nB+\dfrac{2nP_T^2T}{s\times 4.18}}{4\sigma T^3 A(e_1+e_2)} \text{ ohms}, \quad n^2 = \frac{4\sigma T^3 A'(e_1+e_2)}{\dfrac{8B}{R_t}+\dfrac{2P_T^2T}{4.18(R_G+R_t)}}, \tag{25}$$

and Eq. (23) becomes

$$R_t = \left(\frac{R_G n^2 B}{4\sigma T^3 A'(e_1+e_2)}\right)^{1/2} \text{ ohms}, \tag{26}$$

if the Peltier heat is neglected. A solution of Eqs. (25) and (16) if the Peltier heat is neglected is $R_t = R_g$; however, since n must be an integer this solution is only approximate, but it can be put in Eq. (25), where R_g is the smallest convenient galvanometer resistance, and the nearest integral value of n thus found can be substituted in Eq. (26) to give the optimum R_t to be finally substituted in Eq. (24).

The sensitivity of thermocouples should be increased by operating them at very low temperatures. According to Eq. (20) or (24) by appropriately increasing R_t, the maximum possible gain from a single receiver thermocouple at liquid oxygen temperature would be about 5 times if the value of P_T remains constant. The value of P_T can be doubled by using Bi+11% Sb against Bi+10% Sn at liquid oxygen temperature; however, experiments by the author seemed to indicate that the gain in P_T was somewhat off-set by an increase in the Wiedemann-Franz constant, B. For a large receiving area the optimum number of junctions to be used in series is reduced by operating the thermocouple at lower temperature.

[5] C. H. Cartwright, Rev. Sci. Inst. **1**, 592 (1930).

II. Thermocouple with Vacuum Tube Amplifier

The use of vacuum tubes for amplifying the current from a thermocouple is impractical. A vacuum tube primarily detects voltage and is limited to about 1×10^{-6} volts because of the shot-effect. A galvanometer is therefore more sensitive for detecting the thermocouple voltage. Currents as low as 1×10^{-18} amp. are detected with a vacuum tube but only by having this small current flow through a very high resistance in order to gain a detectable change in voltage.

III. Radiomicrometers

The theoretical natural observation limit of a vacuum radiomicrometer due to Brownian motion is the same as was determined for a thermocouple with a separate galvanometer. The curves in Fig. 2 show that the gain in sensitivity by combining the thermocouple and galvanometer into one instrument to form a radiomicrometer can not be very great. The gain by eliminating the resistance of the leads between the galvanometer coil and a separate thermocouple is probably offset by the loss in flexibility, difficulty in removing mechanical vibrations, and the construction of a more costly and a more specialized instrument.

The greater deflections of a radiomicrometer over a thermocouple with a separate galvanometer reported by some investigators may be attributed to a more favorable choice of the two instruments.

In many reports, the sensitivity of the radiomicrometers have undoubtedly been greatly overestimated. The minimum detectable rise in temperature of the thermocouple receiver can be found by dividing equation (6) by the thermoelectric power of the elements; thus,

$$\Delta T_{\text{min.}} = \frac{4.48 \times 10^{-10}}{P_T}\left(\frac{R_c}{t_0}\right)^{1/2} \text{°C}. \tag{27}$$

For a thermoelectric power of 120 μv/°C, a total critical damping resistance of 20 ohms, and a galvanometer period of 20 sec., the minimum detectable rise in temperature is 4—10^{-6}°C. Similar radiomicrometers, in the literature, are described as being able to detect usually 1×10^{-6}°C, sometimes 1×10^{-7}°C, and in one instance 95×10^{-10}°C. These values were probably arrived at by extrapolation, and the galvanometer was not required to be critically damped.

For most work, the maximum sensitivity of a radiomicrometer measured either by the size of the deflections or by the minimum energy detectable should consist of a galvanometer coil of a single turn, a thermocouple of the resistance and number of junctions as calculated by the equations given for thermocouples, and a magnetic field of the correct size to critically damp the instrument.

The combination of a radiomicrometer and a radiometer seems unfavorable for the gain due to the radiometer which requires some gas pressure, is more than off set by the loss in the sensitivity of the thermocouple by not having the vacuum sufficiently high.

Theoretically it should be possible to measure about $5\times3^{1/2}$ as much energy by operating a simple receiver radiomicrometer at liquid oxygen temperature if the values of B and P_T remain constant. This gain in sensitivity is due to cutting down the loss by radiation from the receiver, lessening the Peltier effect, and since the whole instrument is at the low temperature the average Brownian motion fluctuations are also decreased.

IV. Vacuum Bolometer with a Galvanometer

Radiant energy can be measured by allowing it to heat and thereby change the resistance of one arm of a Wheatstone bridge circuit. A factor of about 10 is gained by operating the bolometer receiver in a vacuum to remove the cooling effect of the air and the fluctuations due to air currents. A bolometer can be made compensating without any loss in sensitivity by having identical receivers on the two bridge arms 1 and 2 in Fig. 4.

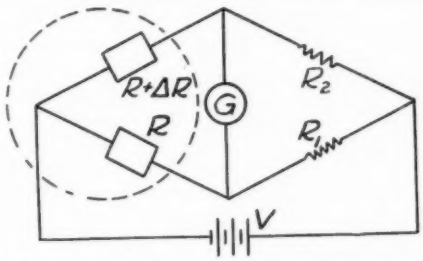

Fig. 4. Vacuum bolometer with galvanometer detector.

The current through the galvanometer for an increase of ΔR in the bolometer when the four arms of the bridge circuit are the same ($R=R_2$) is

$$i_G = \frac{V\Delta R}{4R(R+R_G)+\Delta R(2R_G+3R)} \text{ amps.} \tag{28}$$

The galvanometer deflections are therefore linear to better than the percentage change in the resistance of the bolometer receiver. When the percentage change in the resistance is sufficiently small, the current through the galvanometer is

$$i_G = \frac{V\Delta R}{4R(R+R_G)} \text{ amps.} \tag{29}$$

It will be found desirable to have the resistance of the bolometer receiver sufficiently large so that the heat lost by conduction can be neglected compared with the heat lost by radiation. This condition allows a given amount of energy to raise the temperature of the receiver higher and to give it approximately a uniform temperature. If the receiver is considered to be at an absolute temperature T and only to lose heat by radiation, the following equation holds for the equilibrium state:

$$\text{heat gained} = \text{heat lost in gm}\cdot\text{cal./sec.}$$

$$\epsilon + \frac{(i-\Delta i)^2(R+\Delta R)}{4.18} = 4\sigma T^3 A\Delta T + \frac{i^2R}{4.18}. \tag{30}$$

If only first order terms are considered,

$$\epsilon = \frac{V^2 \Delta R}{4 \times 4.18 R^2} + 4\sigma T^3 A \Delta T \text{ gm} \cdot \text{cal./sec.} \tag{31}$$

The radiant energy, ϵ, increases the temperature and therefore the resistance of the receiver and thereby decreases the heating effect of the battery current; hence the second term in Eq. (31).

If α is the temperature resistance coefficient and ΔT the increase in the temperature of the bolometer receiver,

$$\Delta R = R\alpha\Delta T. \tag{32}$$

The minimum amount of radiant energy detectable with a bolometer can be found by combining Eqs. (11), (29), and (31), thus,

$$\epsilon_{\text{min.}} = \left(\frac{V^2\alpha}{4 \times 4.18R} + 4\sigma T^3 A\right) \frac{4.48 \cdot 4 \cdot 10^{-10}(R + R_G)^{1/2}}{\alpha V t_0^{1/2}} \frac{\text{gm} \cdot \text{cal.}}{\text{sec.}}. \tag{33}$$

Just as for thermocouples, the resistance of the galvanometer should be small.

The optimum voltage with which to operate the bridge can be found by differentiating Eq. (33) with respect to V, thus:

$$\frac{\partial \epsilon_{\text{min.}}}{\partial V} = 0; \quad \frac{V^2}{4 \times 4.18R} = \frac{4\sigma T^3 A}{\alpha} \frac{\text{gm} \cdot \text{cal.}}{\text{sec.}}. \tag{34}$$

If $R + R_G = sR$, where s is given for the particular galvanometers to be used or if s is made as small as convenient if the magnetic field can be adjusted to make the galvanometer critically damped, the maximum of Eq. (33) can be found by differentiating it with respect to R to give:

$$\frac{\partial \epsilon_{\text{min.}}}{\partial R} = 0; \quad \frac{V^2}{4 \times 4.18R} = \frac{4\sigma T^3 A}{\alpha} \text{ gm} \cdot \text{cal./sec.} \tag{34}$$

Eqs. (33) and (34) can be combined to give:

$$\epsilon_{\text{min.}} = 4 \times 4.18 \times 10^{-10} \left[\frac{4\sigma T^3 A(1 + R_G/R)}{4.18\alpha t_0}\right]^{1/2} \text{ gm} \cdot \text{cal./sec.} \tag{35}$$

The heat supplied by the battery is equal to

$$\frac{V^2}{4 \times 4.18R} \text{ gm} \cdot \text{cal./sec.} \tag{36}$$

which appears in Eq. (34). The loss of heat by the receiver is

$$\sigma A(T^4 - T_0^4) \text{ gm} \cdot \text{cal./sec.}$$

where T_0 is the temperature of the surroundings. If dT is taken as equal to $T - T_0$,

$$\frac{V^2}{4 \cdot 4.18R} = \frac{4\sigma A T^3}{\alpha} = 4\sigma A T^3 dT - 6\sigma A T_d^2 T^2 + \cdots \tag{37}$$

and the optimum value of dT is therefore of the order of

$$dT = 1/\alpha \text{ °C}. \tag{38}$$

The value of T for maximum sensitivity would therefore be the temperature of the receiver with no battery current plus the temperature $1/\alpha$. For platinum, $\alpha = 0.003$ so $dT = 333$°C, for nickel $\alpha = 0.006$ so $dT = 167$°C.

If $T = 460$°C, $A = 1$ mm², $\alpha = 0.006$, $t_0 = 1$ sec., and $R_G = R/10$, which would hold for a nickel bolometer operated at room temperature under ideal conditions, the minimum radiant energy as calculated by Eq. (35) would be $\epsilon_{\text{min.}} = 2.3 \times 10^{-11}$ gm·cal./sec. An ideal bolometer would have just about the same sensitivity as a thermocouple; however, it is obvious that the battery current would have to be maintained very constant in order to detect an increase in temperature of the order of 10^{-6}°C when the battery current is heating the receiver over a hundred degrees. Fluctuations in the battery current have two effects. The sensitivity is proportional to the change in voltage and can therefore be neglected. The other effect is more serious unless the two receivers are identical and therefore completely compensating for the heating of the receiver due to the current necessary to operate the bridge is proportional to the square of the voltage. A very constant decrease in the battery voltage should not be serious but fluctuation especially of a period t_0 would be destructive for delicate measurements.

The sensitivity of a bolometer is almost independent of the resistance of the receivers; therefore, the assumption is justified that the loss of heat by conduction could be made negligible compared with the loss of heat by radiation.

The time t_e for the bolometer receiver to reach 99% of its equilibrium temperature if the loss of heat by conduction is negligible is

$$t_e = 4.61mc/4\sigma T^3 A \text{ sec.} \tag{39}$$

where mc is the heat capacity of the receiver. The time t_e should be much smaller than the period t_0.

It may be of interest to apply the formulas to a bolometer built by G. Leimbach[6] which had a high sensitivity as measured by the deflection of the galvanometer. With a period of 10 sec. a deflection of 200 cm was produced by a meter candle. The bolometer receiver was made of platinum 0.025 mm wide, 0.00028 mm thick, and 12 mm. long and had a resistance of 165 ohms. The bridge was operated on about 0.1 volt. The formulas are especially applicable to this bolometer for the resistance of the receiver is large enough so that most of the heat is lost by radiation. According to Eq. (33), this bolometer would have a sensitivity of $\epsilon_{\text{min.}} = 1.2 \times 10^{-9}$ gm·cal./sec. when used with a galvanometer of 1 sec. period and a resistance of 165 ohms. A good thermocouple would give one hundred times more sensitivity with a

[6] G. Leimbach, Ann. d. Physik **33**, 308 (1910).

receiving area of 0.63 mm². By Eq. (37), the battery current would heat the receiver 4.2°C above the temperature of the room. If the receivers were not compensating, the allowable fluctuation in voltage would be 8×10^{-6} volt. By Eq. (39), 1.6 sec. would be required for the receiver to reach 99% of its final temperature.

The optimum design for a bolometer circuit was considered at first to have the four arms of the bridge equal.[7] Later considerations[8,9,10] showed that a larger galvanometer deflection was produced by having the balancing arms of the bridge 4 to 20 times the resistance of the receivers and the galvanometer resistance 0.6 to 4 times the resistance of the receivers.

When the battery current heats the receiver $1/\alpha$ degrees above the room temperature, the optimum condition exists that R should equal R_2. When less battery current is used there can be a gain in sensitivity by making R_2 greater than R.

It seems reasonable to conclude that at present the bolometer is not as suitable for delicate radiometric measurements as a thermocouple.

V. Vacuum Bolometer with Vacuum Tube Amplifier

The objection to the use of a vacuum tube for measuring the thermocouple current might not apply to a bolometer for the resistance could be made very large in order to gain a large voltage drop.

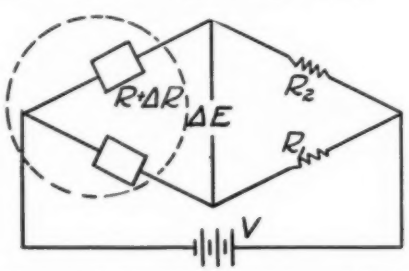

Fig. 5. Vacuum bolometer with vacuum tube detector.

The voltage to be detected by the vacuum tube for the bolometer and bridge shown in Fig. 5 is

$$\Delta E = \frac{VR_2\Delta R}{(R+R_2)(R+R_2+\Delta R)} \approx \frac{VR_2\Delta R}{(R+R_2)^2} \text{ volt} \tag{40}$$

and taking $R = R_2$ for simplicity,

$$\Delta E = V\Delta R/4R \text{ volt}. \tag{41}$$

By Eq. (32),

$$\Delta E = V\alpha\Delta T/4 \text{ volt}. \tag{42}$$

[7] Lummer and Kurlbaum, Ann. d. Physik **46,** 204 (1892).
[8] Abbot, Astrophys. J. **18,** (1903).
[9] W. W. Coblentz, B.B.S. **4,** 391 (1908).
[10] W. W. Coblentz, B.B.S. **9,** 7 (1913).

Since the resistance must be high, equations (30) and (32) can be combined thus,

$$\epsilon = \left(\frac{V^2\alpha}{4 \times 4.18R} + 4\sigma T^3 A\right)\frac{4\Delta E}{V\alpha}\ \frac{\text{gm}\cdot\text{cal.}}{\text{sec.}}. \tag{43}$$

Eqs. (34), (37), and (38) apply equally well for this bolometer so that Eq. (43) becomes,

$$\epsilon_{\text{min.}} = \frac{32\sigma T^3 A\Delta E_{\text{min.}}}{V\alpha}\ \frac{\text{gm}\cdot\text{cal.}}{\text{sec.}}. \tag{44}$$

Using $E_{\text{min.}} = 10^{-5}$ volt,[11,12] $T = 460°$Abs., $A = 1$ mm², and $\alpha = 0.006$, Eq. (44) becomes:

$$\epsilon_{\text{min.}} = 17.1 \times 10^{-8}/V\ \text{gm}\cdot\text{cal./sec.} \tag{45}$$

For $\epsilon_{\text{min.}} = 5 \times 10^{-10}$ gm·cal./sec., $V = 142$ volts. R would be 1.4×10^6 ohms and dT would be 167°C.

The greatest hope of using a bolometer with a vacuum tube for radiometric work lies in making the receiver of some material, probably nonmetallic, that has an unusually high temperature resistance coefficient. It might be possible to operate the bolometer at some temperature at which some material has a very high temperature resistance coefficient. Such a material might be evaporated in a thin layer onto a thin mica receiver.[13,14]

VI. Expansionmeter

It is conceivable that the linear thermal expansion of a metal receiver might be measured to determine the quantity of radiant energy falling upon the receiver. Although the linear extension would be very small, some device such as a thermorelay might be employed for magnifying the effect to make it easily measurable. Without giving any details for the construction, any device for measuring radiant energy by measuring the linear extension of the receiver due to thermal expansion will be called an expansiometer. The natural observation limit of such an instrument will be determined to see whether it would have any possible advantages over other devices. If the receiver has an area A, length l, cross-sectional area perpendicular to the length A', thickness t, and a modulus of elasticity y, and the elongation of the receiver due to Brownian motion is Δl, the potential energy can be set equal to the average Brownian motion energy thus,

$$\frac{\overline{F\Delta l}}{2} = \frac{yA'\overline{\Delta l^2}}{2l} = \tfrac{1}{2}kT. \tag{45}$$

Therefore, the root mean square elongation of the fluctuating length is

$$\sqrt{\overline{\Delta l}} = \left(\frac{kTl}{yA^1}\right)^{1/2}. \tag{46}$$

[11] A. V. Hill, Rev. Sci. Inst. **4**, 72 (1926).
[12] J. B. Johnson, Phys. Rev. **32**, 97 (1928).
[13] H. C. Burger and P. H. van Cittert, Zeits. f. Physik **66**, 210 (1930).
[14] C. H. Cartwright and John Strong, Rev. Sci. Inst. **2**, 189 (1931).

The elongation due to a rise in temperature of ΔT is

$$\Delta l = \beta l \Delta T, \tag{47}$$

where β is the coefficient of thermal expansion for the receiver.

If the minimum measurable effect is again taken arbitrarily to be equal to four times the amount excited by the average Brownian motion fluctuations, the minimum detectable rise in temperature is

$$\Delta T_{\text{min.}} = \frac{4}{\beta}\left(\frac{kT}{yA'l}\right)^{1/2} = \frac{4}{\beta}\left(\frac{kT}{yAt}\right)^{1/2} °\text{C}, \tag{48}$$

where $A'l$ or At is the volume of the receiver.

The minimum detectable rise in temperature of a receiver 1 mm² area and 0.001 mm thick of different metals as calculated from Eq. (48) is tabulated in Table I.

If the receiver is considered only to lose its energy by radiation, the minimum amount of radiant energy detectable as calculated by equation, $\epsilon = 4\sigma T^3 A \Delta T$, (43) ,is tabulated in Table I. The time for the receiver to reach 99% of its equilibrium temperature as calculated by Eq. (39) is also listed.

TABLE I. *Expansiometer with a receiver 1 mm² area and 0.001 mm thick.*

Material	$\Delta T_{\text{min.}}$°C	$\Delta\epsilon_{\text{min.}}$ gm·cal./sec.	t_e sec. for 99%
Aluminum	2.7×10^{-5}	3.7×10^{-11}	1.9
Gold	4.6	6.3	2.0
Copper	3.5	4.7	2.75
Steel	3.0	4.1	3.6
Nickel	3.0	4.1	3.2

Table I shows that for the metals chosen an expansiometer could not be constructed that would have the sensitivity of a thermocouple. The calculations have been made for a vacuum expansiometer under the most ideal conditions for the receiver is assumed to not lose any of its heat by conduction and the energy of Brownian motion of $\frac{1}{2}kT$ is too small for the two degrees of rotation of the receiver which would be measured as an elongation have been omitted.

The effect of Brownian motion is decreased by making the receiver thicker and also the time for taking readings is increased. The sensitivity of an extensiometer by increasing the thickness of the receiver should increase as the square root of the time to take observations just as was found to be true for a critically damped galvanometer.

It can be concluded that a thin bimetalic receiver would not be useful for making accurate radiometric measurements.

VII. RADIOMETER

The sensitivity of a radiometer as determined only by the size of the deflection produced by a measurable quantity of radiant energy can easily be made ten or even a hundred times more than is possible with a thermocouple and a moving coil galvanometer, but the Brownian motion fluctuations will be

so large that they can be observed directly without the use of a thermorelay amplifier as is usually necessary for the other instruments.

The torque, in equation (1) produced by a quantity of radiant energy $\epsilon_{\text{min.}}$ falling on a radiometer receiver can be taken as

$$F = s\epsilon_{\text{min.}}r = \Delta P \cdot Ar \text{ dyne} \cdot \text{cm}, \tag{50}$$

where r is half the distance between the centers of the pair of receivers, ΔP is the radiometric pressure caused by $\epsilon_{\text{min.}}$, and s is a proportionality factor which will depend on the gas pressure, the construction of the radiometer, and the size and shape of the receivers. The value of s is equal in magnitude to the total radiometric force in dynes divided by the radiant energy absorbed in erg/sec.

A solution to Eq. (1) is

$$(\delta\theta)_{\text{min.}} = s\epsilon_{\text{min.}}r/K \text{ rad}. \tag{51}$$

The period is given by Eq. (3) and the necessary friction for critically damping the radiometer according to Eq. (2) is

$$D = 2(IK)^{1/2} \text{ dyne} \cdot \text{cm} \cdot \text{sec.}, \tag{2}$$

where D will depend on the gas pressure, the construction of the radiometer, and the size and shape of the receivers.

Eqs. (3), (9), (10), (51), and (2) can be combined to give

$$\epsilon_{\text{min.}} = \frac{4}{sr}\left(\frac{\pi kTD}{t_0}\right)^{1/2} \frac{\text{erg}}{\text{sec.}}. \tag{52}$$

The sensitivity of a critically damped radiometer is therefore proportional to the square root of the period just as for a galvanometer and an expansiometer. The damping resistance D decreases as the area of the receivers is made smaller; hence the energy to be measured should be concentrated onto as small a receiver as is convenient. Also, the value of s increases for small receivers.

For a galvanometer the best values for t_0 and R_e can be chosen and the magnetic field can be adjusted to make the galvanometer critically damped. For a radiometer, the corresponding procedure would be to choose t_0 and r and adjust the gas pressure to make the radiometer critically damped; however, the value of s and D both depend on the gas pressure and must be considered. The value of s as a function of pressure can be determined experimentally for a given radiometer for it will be directly proportional to the magnitude of the deflections of the radiometer produced by a known amount of energy as the pressure is varied. As the gas pressure is increased, the value of s steadily increases and reaches a maximum at a pressure between 0.01 and 1 mm of Hg and then the value of s steadily decreases for higher pressures.[18,19,20] The shape of the curve and the position of the maximum depend

[18] S. Smith, Proc. of N. A. of S. **16,** 373 (1930).
[19] I. D. Tear, Phys. Rev. **23,** 641 (1924).
[20] M. Knudsen, Ann. d. Physik **6,** 129 (1930).

on the construction and design of the radiometer and the gas used. Since the value of D is decreased by lowering the pressure, Eq. (40) shows that a radiometer should be operated at a pressure lower than the pressure corresponding to the maximum value of s. Fortunately, this condition can be satisfied for radiometers of practical design.

The radiometer pressure and therefore s as a function of pressure under ideal conditions has been determined theoretically and experimentally by M. Knudsen.[20] His recent paper treats very completely the radiometric pressure for the high and low pressure region as well as the intermediate region in which the radiometric pressure reaches its maximum value. His formulas are particularly adaptable for radiometers of the double vane type. The radiometric pressure Δp for an increase in the temperature of the receiver ΔT is given approximately by Knudsen to be

$$\Delta p = \frac{(a' - a'')\Delta T}{4T(cb)^{1/2}\left(\frac{1}{P(cb)^{1/2}} + P(cb)^{1/2} + 1\right)} \frac{\text{dyne}}{\text{cm}^2}, \tag{53}$$

where $(a'-a'')$ is the "akkommodationskoeffizient" which is 0.4898 for helium and 0.363 for hydrogen, $c^{1/2}$ is 0.0105 for helium and 0.0149 for hydrogen, b is the width of a rectangular receiver in cm and p is the gas pressure in dynes/cm^2. The radiometric pressure reaches its maximum where $P_{\max.} = 1/(cb)^{1/2}$, so that the maximum radiometric pressure by Eq. (41) is

$$\Delta P_{\max.} = \frac{(a' - a'')\Delta T}{12T(cb)^{1/2}} \frac{\text{dyne}}{\text{cm}^2}. \tag{54}$$

If the receiver is heated an amount ΔT by an amount ϵ of radiant energy falling on the receiver, the energy is lost by radiation and conduction and convection of the gas so that the following equation holds for the equilibrium state:

$$\epsilon = (4\sigma AT^3 + CA)\Delta T \text{ erg/sec.}, \tag{55}$$

where $CA\Delta T$ is the energy lost by the gas and $\sigma = 5.7 \times 10^{-5}$.

Eqs. (50), (54) and (55) can be combined to give:

$$s_{\max.} = \frac{\Delta P_{\max.} A}{\epsilon} = \frac{(a' - a'')}{12T(cb)^{1/2}(4\sigma T^3 + C)} \frac{\text{sec.}}{\text{cm}} \tag{56}$$

and therefore Eq. (52) becomes

$$\epsilon_{\min.} = \frac{4 \times 12T[cb\pi DkT(4\sigma T^3 + C)]^{1/2}}{r(a' - a'')t_0^{1/2}} \frac{\text{erg}}{\text{sec.}}. \tag{57}$$

Eqs. (2), (3) and (57) can be combined to give

$$\epsilon_{\min.} = \frac{4 \times 12T(cb\pi kTK)^{1/2}(4\sigma T^3 + C)}{r(a' - a'')} \frac{\text{erg}}{\text{sec.}}, \tag{58}$$

where the value of K and r must be considered as chosen so that the radiometer will be critically damped at the pressure where s is near its maximum value for the desired period.

The magnitude of C was determined to be approximately eight times as large as $4\sigma T^3$ for room temperature. This was determined by Eq. (56) for small radiometers and also by finding the increase in the sensitivity of thermocouples (with receivers of the same size as the radiometer receivers) when the pressure was lowered from the pressure needed for the radiometer to a high vacuum. The thermocouples were constructed so that the loss of heat by conduction through the wires was small as compared with the loss by radiation and the receivers were comparatively thick so that the temperature of all parts of the receiver was the same.

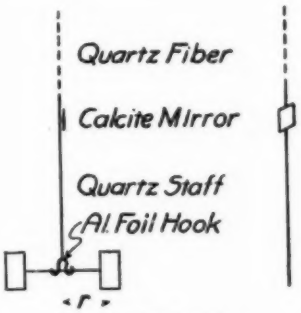

Fig. 6. Radiometer.

With the assistance of Mr. W. Hoch, a radiometer was constructed as shown in Fig. 6. Five different radiometer receivers were hung in the aluminum hook and tested.

One quartz fiber had a restoring force of 2.2×10^{-6} dyne·cm. The deflection on a meter scale corresponding to $\frac{1}{2}kT$ of Brownian motion was 0.13 mm; therefore, a measurable quantity of energy would have to cause a deflection of 0.5 mm. The fluctuations only depended on the constant of the fiber and not on the radiometer used.

One radiometer with double vane mica receivers 0.7 mm$\times$1 mm and r equal to 3.5 mm had a moment of inertia of 3.3×10^{-6} gm·cm^2. The period was 8 sec. and critical damping occurred at a pressure slightly below the maximum sensitivity. The maximum value of s for this radiometer was 5.6×10^{-7} sec./cm and the minimum energy that could be detected by a single reading was 1.3×10^{-10} gm·cal./sec. A thermocouple with a receiving area of 0.7 mm^2 and a galvanometer with an 8 sec. period should be over twenty times more sensitive.

HIGH VOLTAGE CATHODE RAY AND X-RAY TUBES AND THEIR OPERATION

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(Received July 20, 1931)

Abstract

The following recommendations are made as bearing upon tube design. The glass used should be free from such elongated gas bubbles as are to be found in drawn tubing —only mold-blown tubing should be employed. The larger the bulb the better and, for use in air, thickness of bulb wall is conducive to good operation. The anode arm should be so dimensioned with respect to the anode as to provide a rather long and relatively narrow space between the two, as this helps to keep reflected electrons from getting too far into the anode arm and so building up a destructive potential gradient in the glass. While under ideal conditions a cathode arm could be dispensed with, it is, in general, better to have one and to give it essentially the design of the anode arm. For currents of as much as several milliamperes, a hollow anode is desirable, as it reduces the number of reflected electrons which get into the anode arm. It also lends itself to the easy attainment of adequate x-ray protection. With a target consisting of a wrought tungsten face attached to a water-cooled mass of copper, the tungsten face must be thick enough to avoid local melting of the copper at any point behind it. If the tube is intended for operation on intermittent current, the temperature gradient between the acting face of the target and the cooling medium must not be too high, as otherwise the forces of heat expansion and contraction will in time wreck the target. To avoid troublesome field currents, the electrodes should have their cooperating ends facing one another rather than being placed one within the other. They should consist of metal which has had a thorough degassing treatment. All sharp edges and corners should be avoided in both cathode and anode structures. The canal systems caused by disruptive discharges in the glass, resulting from field currents, resemble those produced in various colloidal materials under cathode-ray bombardment in air. During assembly great care must be exercised to keep all parts scrupulously clean, and during exhaust equal care must be taken to avoid sputtering, as otherwise a troublesome conducting layer will be formed on the inside of the bulb. Cascading may be resorted to for voltages higher than can be sustained by a single section, and can apparently be made to take care of any voltage which can be generated. With a hollow anode, magnetic focusing may be required, to reduce the size of the cathode ray beam, and with a cascade tube system, it is better to apply it at the anode end rather than at an intermediate electrode. Reference is made to several forms of high voltage generator, including a transformer without rectifier, a full-wave transformer-kenotron outfit, a constant-potential direct-current outfit and an induction coil. One embodiment of the last named is described in detail. A complete induction coil x-ray outfit is described for 900,000 volts and 5 milliamperes, which has just been installed for experimental therapy at the Memorial Hospital in New York City. In the industrial field, it seems almost certain that such high voltage x-ray equipment will be used for the radiographic examination of thick sections of metal. A tube can be much smaller, for a given voltage, when operating in oil instead of air, and it is predicted that, in future, x-ray or cathode ray tubes for very high voltages will be operated immersed in the same oil with the high voltage source and with no portion of the high voltage circuit exposed to the air. This will make for a great reduction in space occupied and for reduced electrical hazard.

1. Introduction.

THE aim of the paper is to discuss some of the factors bearing upon the behavior of high voltage cathode ray and x-ray tubes and to make certain generalizations based upon our experience in this field.

Attention should be called, at the start, to the fact that rigid adherence to these generalizations is not a requisite to success. If operating conditions are all favorable, one can often get along very nicely with a tube design which, for a slightly different set of conditions, would be entirely unsatisfactory. The idea in making these generalizations is merely to point the way to what seem to be paths of least resistance.

2. Freedom of glass from elongated bubbles.

Drawn tubing should be avoided, as, due to the process of manufacture it contains greatly extended bubbles, or so-called air lines. High potential differences developed between the ends of these bubbles result in puncture of their walls. Mold-blown tubing is free from this defect.

3. Thickness of glass.

For operating in air the thickness of that portion of the glass wall surrounding the co-operating ends of the electrodes, or, in other words, of that portion which is in a strong field, is important. The smaller the bulb, for a given voltage, the thicker should be the wall. The value of a thick layer of solid dielectric is readily shown by starting with a tube having a thin glass bulb, acquainting one's self with its behavior and then casting a relatively thick layer of wax, such as de Khotinsky cement, around the bulb. It will be found that, without the wax, there is a voltage at which one could not operate continuously without puncture. At this voltage, noisy spark discharges will take place over the outer surface of the glass and the tube will set up violent surges in the supply circuit. With a thick wax coating, the surface discharges and surges disappear, and the tube can be operated at a substantially higher voltage than before. A thin coating of wax will not produce the same result, showing that the beneficial effect does not come from merely changing the surface.

4. Size of bulb.

With other conditions adapted to it, the larger the bulb the higher the voltage which can be borne.

5. Design of arms of tube.

It is essential that the size of the anode arm shall be properly adapted to the size of the anode. The inner surface of the bulb is at essentially cathode potential and, for this reason, the anode arm must provide insulation for nearly the entire voltage. There must be a relatively long and narrow space between the anode and the surrounding glass envelope, as, otherwise, electrons reflected from the target will get too far back in the anode arm, and this will result in too high a potential gradient along the glass of the anode arm, with consequent break-down.

With fully rectified current and the best vacuum conditions, the design of the cathode arm is not important; in fact under these conditions one could dispense with a cathode arm. With the sudden liberation of a little gas, however, positive ion bombardment of the glass about the cathode will result in destructive potential gradients at this end of the tube. Or, with incomplete rectification, electrons coming from a hot focal spot on the target, or emitted from the target as field currents, may get into the cathode arm and there set up destructive potential gradients on the surface of the glass. It is therefore, in general, better to have a cathode arm and to give it essentially the same design as the anode arm.

Glass tubing used within the arms to support the electrodes should not extend into the bulb unless such tubing is completely metal-covered, as it will otherwise be subjected to destructive sparking.

6. Freedom from metal deposit on inside of bulb.

For highest voltages this is very important. Its attainment calls for extreme care in the preparation of the electrodes, in the operation of sealing them in, and in the exhaust procedure.

7. Relative position of electrodes with respect to one another.

For highest voltages the electrodes should be spaced apart with their cooperating ends facing one another. This seems much better than having either electrode project into the other. With the former arrangement, there is much less trouble from field currents, due perhaps to more effective cleaning by positive ion bombardment of those portions of the electrode surfaces which are exposed to the highest potential gradients.

8. Use of suitable electrode materials and thorough preliminary degassing.

In this field our work has been greatly assisted by that of Dr. Marshall[1] who has arranged to heat samples of various metals in a very high vacuum, and to collect and analyze the gas given off at different temperatures.

In the case of molybdenum, for example, Dr. Marshall finds that each time, as the temperature is raised, there is at first a rapid evolution of gas, followed later by a marked slowing down in the process. There would be, in general, no complete degassing at the lower temperatures, no matter how long the time. At about 1800°C, Dr. Marshall gets complete degassing of molybdenum, or at least as complete degassing as can be attained by thermal treatment. The composition of the gas given off at different temperatures varies greatly.

He finds that the time required for complete degassing of a molybdenum sample is, within the experimental error, a linear function of the thickness, showing that the process is not confined to the surface but extends throughout the specimen.

That such preliminary heat treatment in high vacuum is of great practical importance is indicated by an experiment in which Dr. Marshall takes a

[1] A. L. Marshall and F. J. Norton, to appear soon in the Jour. Am. Chem. Soc.

sample of molybdenum which has first been completely degassed and then brought out into the air and handled. Upon heating this specimen to 1600°C in a vacuum, it gives up the gas, which it has acquired, immediately. The effect of exposure to air and of handling is then confined entirely to the surface.

Dr. Marshall's work on molybdenum, and other metals, also shows that the gas content of a metal is largely dependent on the metallurgical processes which have been used in its production.

9. Creepage along inner surface of tube from end to end.

This difficulty is not experienced in operating tubes in air, as they will arc-over outside before showing this trouble inside. Tubes built for operation in oil may show this trouble if the bulb is small and the arms short. It may be remedied either by making the bulb larger or the arms longer, or by corrugating (crimping) the bulb.

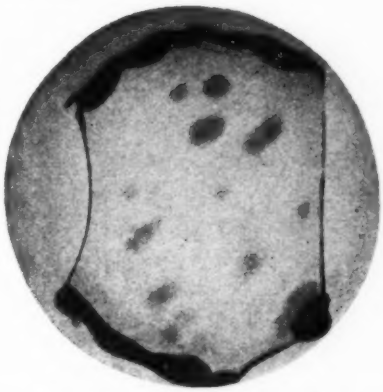

Fig. 1. Oval discolored areas in glass bulb of x-ray tube, resulting from cold-cathode discharges.

10. Cold-cathode effect.

The one factor which, more than any other, limits the voltage which can be used today with a single section tube, is the production of field currents from the cathode to the glass envelope. (Field currents passing between electrodes can be sufficiently reduced by electrode design and the use of adequate spacing.)

The production of field currents going to the glass may be reduced by so designing the electrodes that no portion which is exposed to a strong field shall have too small a radius of curvature. Careful freeing of the entire tube from loose particles, and thorough degassing of the electrodes are also important factors.

These field currents cause local fluorescence of the glass and a permanent color change. The bombarded areas are in general very fixed in position and sharply defined. See Figure 1, which is from a photograph of a section of a tube which has been operated at a voltage high enough to produce severe bombardment of the glass.

So long as nothing but fluorescence can be seen, no damage is done to the glass. But, in addition to a rather uniform fluorescence of the bombarded areas, one may sometimes observe tiny bright yellowish spark discharges within these areas and then, under the microscope, one will find a complicated branching network of tiny canals corresponding to each of these spark discharges. See Figure 2, which is a photomicrograph of a discolored area like those shown in Figure 1. The periphery of the discolored area has been emphasized by the dotted line. The damage is seen to be limited to the discolored area. The canals of such a network all communicate with one or more craters opening into the interior of the x-ray tube. Usually the network all lies essentially in a plane parallel to the inner surface of the tube, but,

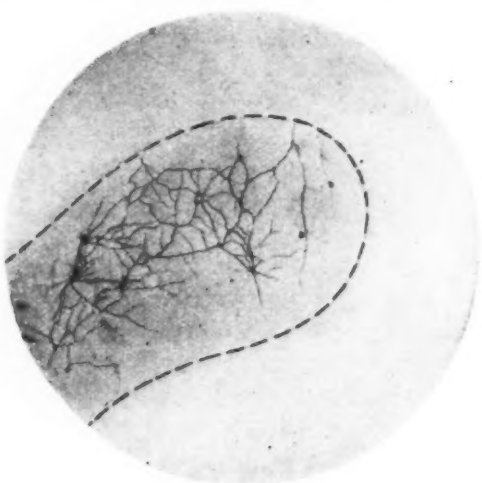

Fig. 2. Photomicrograph of one of the discolored areas in Fig. 1.

in other cases, tiny canals may be found leading from the main network to the outside of the tube.

The canal systems produced by these disruptive discharges in the glass resemble those which are formed in some substances under cathode ray bombardment in the air in front of the window of a Lenard tube. See Figure 3, taken from a paper by Coolidge and Moore,[2] showing the result of cathode ray bombardment, in air, of celluloid at liquid air temperature. This subject calls for further study.

11. Hollow anode conducive to good operation and to ease of securing adequate x-ray protection.

For low milliamperages, it appears to make but little difference in the operating characteristics of an x-ray tube whether the anode is solid or hollow, but as the current is increased the tube with the hollow anode will, in general, be found to behave better than the one with the solid anode. The reason is doubtless to be found in the fact that so many electrons are re-

[2] W. D. Coolidge and C. N. Moore, Jour. Frank. Inst. **202,** 726–728 (1926).

flected from the face of the target and that in the case of the solid anode many of these find their way into the anode arm. A further advantage of the hollow anode consists in the fact that in case the focal spot is overloaded, the metal vapor produced does not get to the glass envelope. Nor should the ions resulting from this metal vapor cause the same runaway effect that they otherwise would, for the reason that they are generated in a region where there is no electric field.

The use of the hollow anode also makes it easier to get adequate x-ray protection, for it can project beyond the outer end of the glass anode arm, where it can be surrounded with any desired amount of lead.

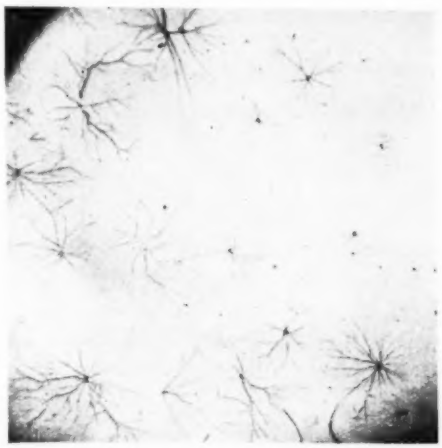

Fig. 3. Resembles Fig. 2 in appearance and is result of disruptive discharges in celluloid under Lenard ray bombardment at low temperature.

12. The target.

If the target is to consist of a tungsten face attached to copper, the face must be thick enough so that, for the focal spot size in question and for the maximum tube load, there will be no point under the focal spot at which the tungsten surface in contact with the copper gets to the melting point of the latter. For if the copper melts locally, it will expand, bulging the tungsten face out at this point, and then on cooling leave a vacuous space. On subsequent use, the tungsten may melt at this point because it is no longer in good thermal contact with the copper.

If the tube is to be operated on an *intermittent* current source, the target must be so designed that the temperature gradient from the focal spot to the cooling medium is not too great, as otherwise the life of the target will be very short. This is due to the forces of expansion and contraction set up as the focal spot is heated and cooled. If, as a result of these forces, the elastic limit of the target metal is exceeded, detailed fracture results and the tearing may gradually extend itself from the focal area right through the target to the chamber containing the water or other cooling medium.

13. Cascading.

Having attained the best design of single-section tube, cascading can then be resorted to for still higher voltages—apparently for any voltage which can be generated.

A 3-section cathode ray tube for operation at 900,000 volts has already been described,[3] and Figures 4 and 5 show a recent 2-section x-ray tube for the same voltage.

14. Magnetic focusing.

With x-ray tubes having hollow anodes, and especially those in which cascading is used, it may be necessary to provide magnetic focusing to control the size of the cathode ray beam at the target. The reason for this is as

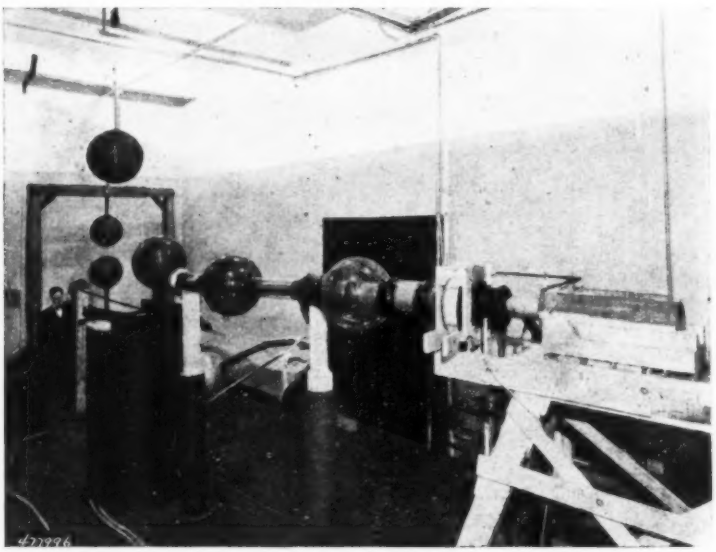

Fig. 4. Two-section x-ray tube with magnetic focusing, operating from induction coil at 900,000 volts and 5 milliamperes.

follows: with a cathode designed to provide as much as several milliamperes of current, the cathode ray beam is divergent after entering the first intermediate electrode. In passing through the electrostatic field between the electrodes of succeeding sections the divergence is reduced, but upon reaching the target the beam is probably too large. It would be, for example, about 10 centimeters in diameter upon reaching the end of the anode arm in the tube shown in Figures 4 and 5.

Magnetic focusing may be applied between sections, but it seems much more satisfactory to apply it at the anode end of the tube, as shown in Figures 4 and 5. The target is here at the end of a metal extension tube which is about 2 feet long and, to produce a focal spot 1 cm in diameter, a current of about 1 ampere is required in a flat coil having 4000 turns.

[3] W. D. Coolidge, Am. Jour. of Roentgenology and Radium Therapy **19**, 324–326 (1928).

The theory of magnetic focusing for flat coils has been developed by Busch.[4] Our experience indicates that the theory holds very closely for the conditions pertaining in the 2-section x-ray tube of Figures 4 and 5. At 460 kv the relation of focal spot size to the current used in the focusing coil is shown by the graph of Figure 8. As tube voltage is raised, the current required in the focusing coil for a given size of focal spot increases. For example, on going from 460 kv to 700 kv, the current required for the minimum size of focal spot increased from 1.0 to 1.1 amperes.

If much energy is to be employed, there is a very real hazard in having the focal spot size manually adjustable, as it makes it easy to so overload the focal spot as to ruin the target. This is especially true in the case of thin

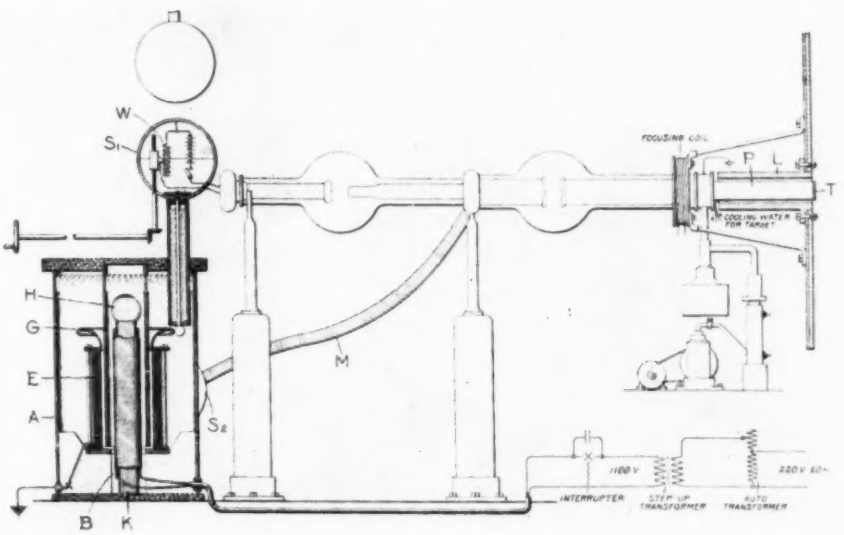

Fig. 5. Diagram of x-ray outfit of Fig. 4.

targets. The hazard can be eliminated by always working with less focusing current than that required for sharpest focusing and using a fixed current-limiting resistance in series with the focusing coil. This resistance should have such a value that, with the lowest tube voltage which is to be employed and with the highest voltage assumed by the line supplying direct current to the focusing coil, the focal spot size is adequate. Then as the focusing current decreases with decreasing line voltage, the focal spot increases in size—a change in the direction of safety. Similarly as tube voltage is raised and with it the energy delivered to the target (assuming that tube milliamperage is kept constant), the focal spot size increases as it should. Further refinements could be introduced, but even without them the conditions are very favorable.

[4] H. Busch, Ann. d. Physik **81**, 974–993 (1926).

15. Adjustable electrostatic focusing member.

It would be difficult to construct a cascade tube as long as that shown in Figures 4 and 5 so accurately that the cathode ray beam would be everywhere exactly central with respect to the axis of the tube. We have therefore found it desirable to make the electrostatic focusing member of the cathode in the first section adjustable. It is supported, as shown in Figure 6, by three metal rods, two of which, r_1, r_2, are shown, each of which can be moved without breaking the vacuum, through the help of three small sylphon tubes, two of which t_1 and t_2, are shown. The required adjustment is quickly made by operating the tube without magnetic focusing while observing a fluorescent screen wrapped around the metal extension chamber at the anode end, or it

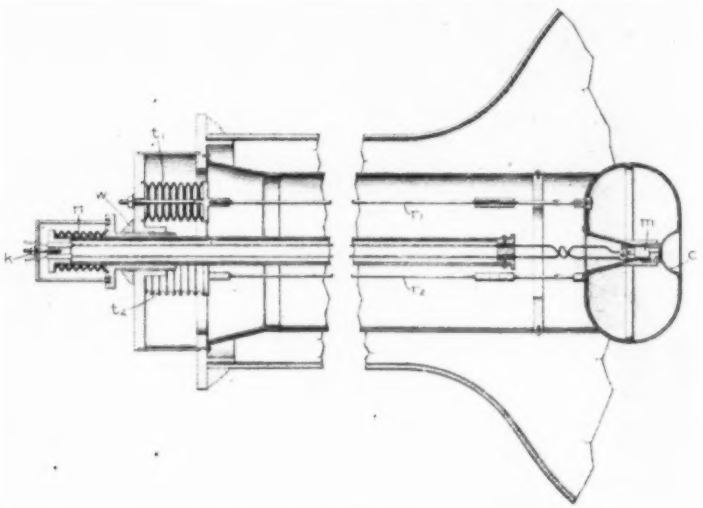

Fig. 6. Details of adjustable cathode structure.

can be made with magnetic focusing, by the help of an x-ray pinhole camera directed at the target.

With proper adjustment of this electrostatic focusing member, none of the beam strikes the intermediate electrode, as is shown by the fact that a milliammeter in series with it indicates no current and that milliammeters placed in circuit at the two ends of the tube read alike.

The focal spot is brought to the exact position desired on the target face by slightly tilting the magnetic focusing coil if necessary.

The cathode filament is rigidly mounted in a molybdenum cylinder, m, which fits loosely in the surrounding copper structure. To permit of adjustment of the setting of the filament relative to the focusing cup, c, without breaking the vacuum, use is made of the sylphon tube, n, and the nut, k. For replacement of a filament, the entire filament assembly may be removed if necessary by letting air into the tube and heating the wax at w.

16. X-ray protection.

In the tube of Figure 5, x-rays are taken out through the target. Protection from most of the x-rays going in the opposite direction is secured by means of the lead cylinder *L*.

To reduce the x-ray production due to electrons coming away from the focal spot the brass tube *P* is lined with aluminum. The tube *P* is made as long and narrow as it is, to reduce the escape of x-radiation in the backward direction.

The target *T*, of this tube, shown in section in Figure 7, consists of a tungsten face *Q*, thick enough to stop 900,000 volt electrons (0.15 mm—calculated from the measured range in air), onto which has been cast a layer of copper *F*, 3 mm thick. Soldered to the back of the copper plate is a brass chamber,

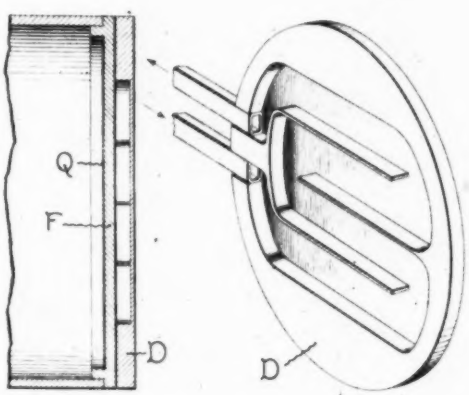

Fig. 7. Details of water-cooled target—x-rays are taken out through it in direction of tube axis.

through which cooling water is circulated. The x-rays have to pass through 3 mm of copper, 3.7 mm of water and 1 mm of brass.

It is of course not necessary to take the x-rays out through the target; they could just as well, and for many purposes better, be taken out from the face of the ordinary thick target, in a direction at right angles to the tube axis.

17. Operation on the pump.

We have done a good deal of work on the pump and without bake-out and with wax joints, simply because it permits of rapid changes in tube design, and not with the thought that this is necessarily the ultimate method of operating high voltage tubes.

18. High voltage sources.

(A) *The induction coil of Figure 5.*

For the production of very high voltage radiation, a type of induction coil has been developed which is relatively cheap and easy to make and very

satisfactory. The authors started with the idea of using solid dielectric between the primary and secondary, but have found it much better to rely mainly on oil. The container A is a Herkolite (paper-resin) tank. The primary B is wound on an insulating tube that surrounds the core K. The secondary E consists of thin coils placed one on top of the other, with paper rings between. The lower end of the secondary is grounded, and the potential difference between secondary and primary then increases as we come up, reaching its maximum at the top of the secondary. With this particular coil arc-over would take place from the top of the secondary to the primary at about 600,000 volts were it not for the split aluminum spinning G, which electrostatically shields the upper end of the secondary and makes it possible to go

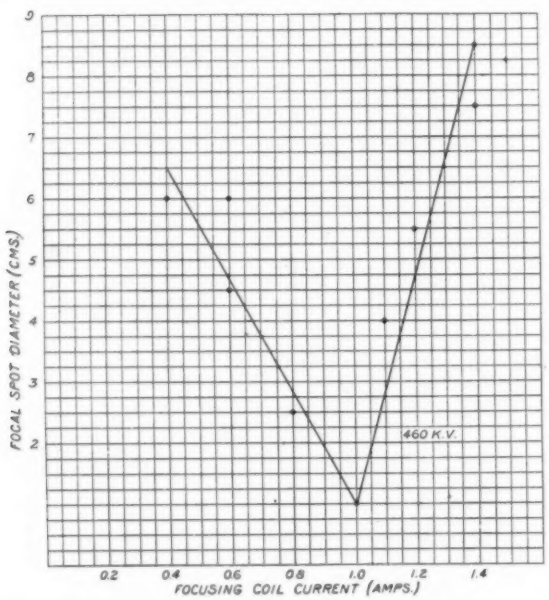

Fig. 8. Graph showing dependence of focal-spot size upon current in magnetic focusing coil.

to about 800,000 volts. At this point, arc-over would take place from the aluminum spinning to the upper end of the core were it not for the spherical shield H, which makes it possible to go up to 900,000 volts. The design of this shield is important, as it has to be electrically conducting and is located where nearly all of the magnetic flux of the core passes through it. If it were a hollow metal sphere of appreciable thickness, most of the energy delivered to the primary would be wasted in the sphere in eddy currents. The construction indicated has been found satisfactory and consists of a wooden sphere overlaid with narrow strips of sheet aluminum placed as shown, and metallically joined at the top to the upper end of the core.

The 900,000-volt lead passes up through an oil bushing to a 20 in. hollow metal sphere S_1, which serves as a container for the storage battery used to light the filament and the remote controlled adjustable rheostat, W, and, at the same time, as a terminal of the measuring sphere-gap. To secure the

required potential for the intermediate electrode of a two-section tube, conductor M and sphere S_2 are connected to the middle of the secondary.

The coil is operated from 1100-volt 60-cycle current, by means of a hydrogen-filled mercury turbine interrupter driven by a synchronous motor.

As one end of the secondary is grounded, it will doubtless be possible to operate two such coils in series to produce nearly two million volts. It seems, furthermore, as though coils could be built in this way for much higher voltages.

For high voltages and currents of not more than a few milliamperes, the induction coil offers the following advantages: It gives such an unsymmetri-

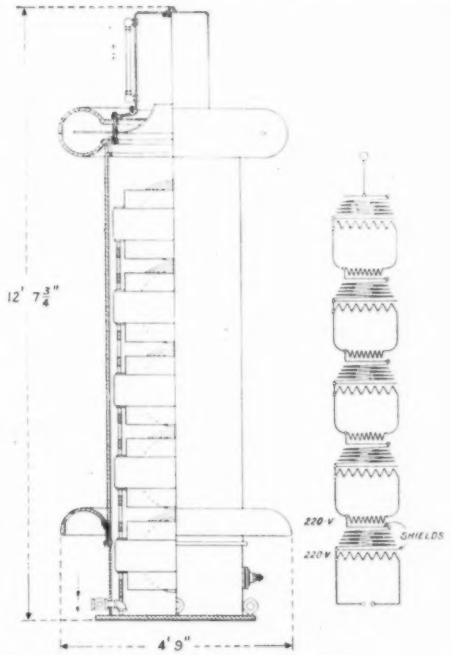

Fig. 9. Elevation of 1,000,000 volt chain-connected transformer, together with circuit diagram

cal wave that, even with a considerable load, the "useful" voltage is higher than the "inverse," and, as a result, and without the need of any complications, the sphere gap indicates the "useful" voltage. Its wave-form permits of the attainment of a given "useful" voltage with a minimum of insulation. The high magnetic leakage, inherent in the open core, tends greatly to diminish the electrical and fire hazards; it also makes it unnecessary to use resistances in series with the measuring sphere-gap. Relatively speaking, the induction coil is of small bulk, simple and inexpensive.

For those applications calling for the maximum allowable x-ray intensity per unit of focal area, the induction coil is at a disadvantage when compared with the transformer, and still more so when compared with a constant-potential continuous-current source, because of the fact that its maximum instantaneous current values are so high compared with the average. Under

heavy duty, it is mainly the maximum instantaneous current value that causes melting and vaporization of the target. Furthermore, the tearing of the target under heavy duty will be greater the greater the temperature fluctuation during the operating cycle and, hence, the greater the difference between the maximum instantaneous and the average current values.

The outfit of Figures 4 and 5 has been installed recently, for experimental therapy, at the Memorial Hospital in New York City.

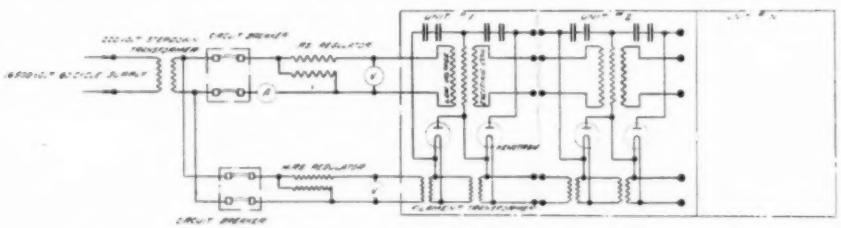

Fig. 10. Circuit diagram of direct-current constant potential generator.

(B) *The transformer without rectifier.*

This is, of course, the simplest type of transformer outfit. Mr. Hendricks, of Pittsfield, has designed a very compact form, shown in Figure 9, and one of them has been built for 1,000,000 volts (max.) It is a chain-connected system in which each element derives its excitation from the one below it. Each element is designed for 200,000 volts (maximum). The oil-filled container is of insulating material, paper-bakelite, and so all high tension bushings are eliminated.

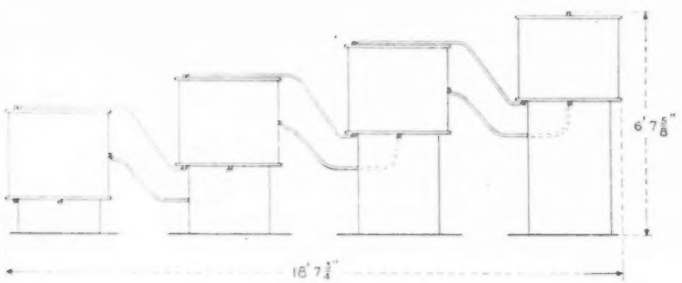

Fig. 11. Elevation showing staircase arrangement of 400,000 volt outfit, as of Fig. 10.

To make the interior accessible, a sub-base, not shown in the figure, is provided, into which the oil from the transformer above can be drained. The casing can then be easily removed.

(C) *Constant potential direct current outfit.*

When given enough capacity, so that voltage ripple is negligible, this has long been regarded as the most ideal source of current. Mr. Hendricks has designed one which looks very attractive. See Figure 10. It is a transformer, kenotron, condenser machine, consisting of 100,000-volt units connected in series. Each unit consists of a transformer, two kenotrons, two kenotron

filament transformers, and two condensers, all mounted in an oil-filled case of insulating material (so that no high voltage bushings are required). A chain-connection of transformers is used, so that each is excited from the one below it in the series. Any number of units may be used to produce the desired voltage.

Fig. 12. Early model of high voltage cathode ray outfit, having tube in same oil with induction coil, designed to hang in tank of oil with cathode end down, and Lenard window at top out of oil and connected to earth.

The units can be mounted one above the other, as in Figure 9, or, for use where the necessary headroom is not available, in a stair-case arrangement, as in Figure 11.

A 400,000 volt outfit of this type has been built.

D. *Transformer-kenotron outfit with "bridge" circuit.*

Mr. Hendricks has also designed a transformer-kenotron outfit in the form of a multiple unit system. Each element is for 140,000 volts (maximum) and

consists of a transformer and four kenotrons for full-wave rectification. A 520,000 volt outfit of this type has been built.

The most attractive feature of generators *C* and *D* is that the potentials at the terminals of the kenotrons are definitely fixed instead of being somewhat indefinite as in the case where kenotrons are connected in series.

19. The oil-immersed type of equipment.

The tube can be much smaller if used in oil, and, looking ahead a little, it would seem most logical to place the high voltage source and the tube close together in the same oil, in some such fashion as shown in Figure 12, in which an induction coil and cathode ray tube are mounted side by side. The tube is intentionally made of the same length as the secondary of the coil, thus facilitating the connection of intermediate electrodes to appropriate points in the secondary. The connections are furthermore so short that they are effectively electrostatically shielded by the secondary and the tube. The cathode end of the tube is at the bottom and the filament is lighted from end turns on the coil. Filament temperature is controlled by means of a small rheostat in the filament circuit, operated from a distance through an insulating shaft. The whole assembly hangs from the top in a tank filled with oil and the upper end is grounded. The tube is readily removable without taking the coil out of the oil. This was an early experimental outfit calling for further development, but the general method of attack still looks very promising.

20. Applications.

It is certainly practical to construct cathode ray and x-ray generating outfits for continuous operation at much higher voltages than are now generally employed.

So far as the therapeutic application is concerned, the question as to whether the radiations produced by higher voltages are or are not more beneficial in the treatment of disease must be left to the medical profession.

In the industrial field, it seems almost certain that such high voltage x-ray equipment will be used for the radiographic examination of thick sections of metal.

For numerous scientific investigations high voltage cathode ray and x-ray outfits will certainly have many important uses.

THE VARIATION IN THE SURFACE TENSION OF GAS-SATURATED PETROLEUM WITH PRESSURE OF SATURATION*

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(Received July 27, 1931)

Abstract

The surface tension of a number of samples of crude petroleum has been measured, by the capillary rise method, as a function of the pressure at which the oil is saturated with gas. Oils and natural gases were used which were obtained from various fields throughout the country. Carbon dioxide, air, and benzene were also used. The oils were saturated with the gases at various pressures up to 2000 pounds per square inch at a temperature of 31°C (88°F), and curves obtained to show how the surface tension varies with the saturation pressure. The results show that in all cases curves of the same general type are obtained, and at 2000 pounds pressure the surface tension has decreased by more than 50 percent. In one case the decrease was as much as 80 percent.

Introduction

THE purpose of this research was to determine quantitatively how the surface tension of petroleum, saturated with gas under pressure, varies with the pressure of saturation. Such data are of some practical importance for it is a well-known fact that with present methods of obtaining oil from the ground only a small portion of the total amount of oil in the sands is recovered. Since surface tension affects the rate of flow through sand and consequently the rate at which oil may be recovered it is of interest to know just how the surface tension varies with the amount of gas in solution, especially since by introducing gas into a partially depleted sand, the amount of gas in solution may be artificially varied.

Method

The capillary rise method of measuring the surface tension was selected as the most suitable for it is very simple and direct yet sufficiently accurate for the purpose. Furthermore, since the measurements must be made inside a chamber under very high pressure it is important that no moving parts be required to be operated from the outside. With this method it is only necessary to make observations through a glass window of the chamber.

* This paper contains results obtained in an investigation on "The Fundamentals of the Retention of Oil by Sand" listed as Project No. 36 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

The suitability of the method is further enhanced by the fact that the angle of contact of all the oils used is zero. This fact was determined by filling a small piece of glass tubing to overflowing with the liquid so that the upper surface was convex. Into this convex surface was dipped a small glass filament so that the capillarity drew the liquid upward around the filament. The angle of contact of this liquid with the glass of the filament could then be easily observed with a microscope and seen to be zero.

The surface tension is given by the formula

$$T = \tfrac{1}{2}(h + a/3)da$$

where T is the surface tension; h the height of lowest part of meniscus above the level of the liquid; a the radius of capillary tube; and d the density of the liquid. The height h is corrected by adding the quantity $a/3$ to account for the weight of the liquid above the lowest part of the meniscus. h was determined by means of a cathetometer, graduated in millimeters, which could be read to tenth millimeters by means of the vernier. To get h, it is not only necessary to be able to set the cathetometer on the meniscus but also on the surface of the main body of liquid. Since the liquid is viewed through a glass window, and since the surface tension pulls the edge of the liquid upward on the inside surface of the window, it is impossible to set the cathetometer directly on the surface. This difficulty was overcome by the usual method of arranging a pointer so that it could be lowered by a screw motion until the point just touched the surface as indicated by the sudden jump of the liquid upward around the pointer due to capillarity. When the liquid was removed the cathetometer could be set on the end of the pointer to get this required level.

In all measurements the meniscus was always allowed to come to the same point on the capillary tube, and at the conclusion of the experiment the radius "a" was determined by breaking the tube at this point and measuring it directly. In this way any error due to variation in the inside radius of the tube along its length was completely avoided.

Since the density d varies considerably with the saturation pressure it is necessary to make a separate determination of d as a function of the pressure. For this purpose a bulb of known volume was suspended from a spring and immersed in the saturated liquid. By calibrating the spring with known weights and measuring the extension when the bulb was immersed in the liquid at various saturation pressures the density change could be easily calculated. By adding this change in density to the density at atmospheric pressure (as determined by a Mohr balance) the absolute value of the density as a function of the pressure is found.

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. It consists essentially of two steel chambers, one for mixing the oil and gas to complete saturation, and one for measuring the capillary rise. The mixing chamber is provided with a motor-operated rotary stirrer consisting of a paddle fastened to a rotating shaft extending through the top of the chamber to the outside

through a large packing gland. The measuring chamber contains the capillary tube and pointer, both visible through the glass window in front. The capillary tube and pointer are illuminated by shining light in through the window from the front and reflecting from a mirror placed against the back of the chamber. The pointer which is used, as explained above, to obtain the level of the liquid in the chamber consists of a pointed shaft extending through the top of the measuring chamber through a packing gland. The packing nut has an elongated head with a hole through the center which is tapped to fit the

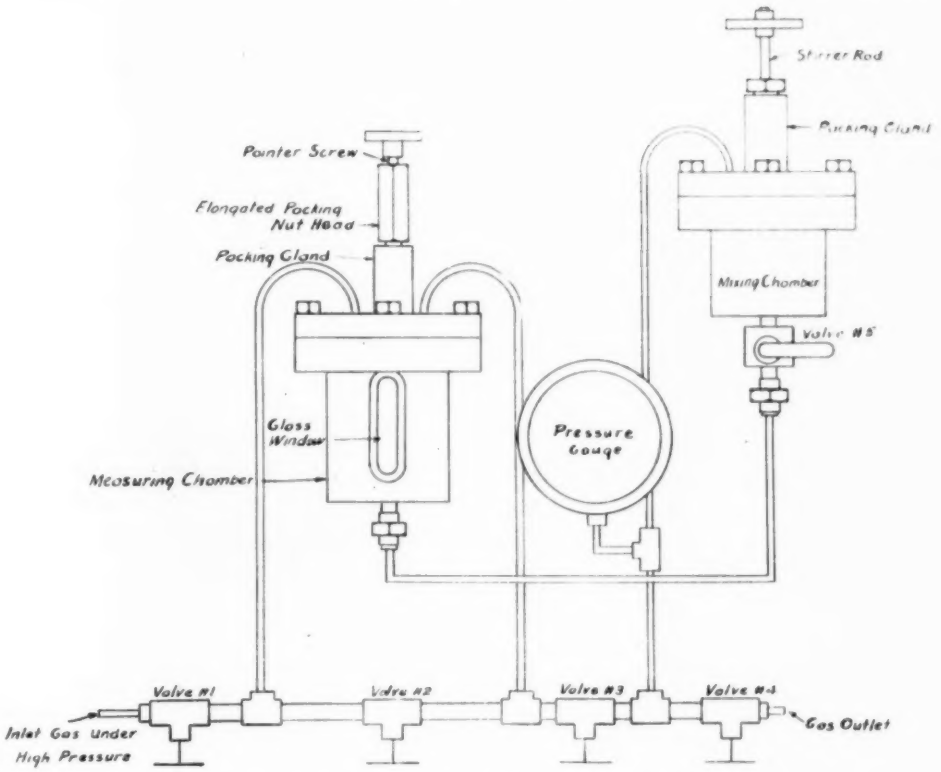

Fig. 1. Diagram of apparatus for measuring the surface tension of oil at high pressures.

threads on the pointer screw. Thus by turning the pointer screw it may be raised or lowered through a range determined by the threaded portion of the packing nut head. The tops of both chambers are fastened rigidly to a wooden frame while the bottom portions are removable by taking out the bolts holding them to the top. The joint between the two parts of each chamber is made gas tight by means of a lead washer (made from 30 ampere fuse wire) fitting into V-shaped grooves turned into the abutting surfaces.

The mixing chamber is at a higher level than the measuring chamber so that after the oil is thoroughly saturated in the former it may be allowed to run by gravity into the latter when valve No. 5 is opened. This valve is a specially constructed leak-proof steel stopcock. The copper tubing connect-

ing the two chambers is easily removable for cleaning purposes by taking apart the two unions shown in the figure.

There are two connections by means of copper tubing through the top of the measuring chamber. The tube leading to the left side of the chamber in the figure connects, on the inside, to the top of the capillary tube, while the tube on the right merely opens into the inside of the chamber. By this arrangement as long as valve No. 2 is open the pressure above the meniscus in the capillary tube is the same as in the surrounding chamber. Between successive measurements, however, it is necessary to force out the liquid remaining in the capillary tube and this may be done by closing valve No. 2 and opening valve No. 1 thus admitting gas through the capillary tube. It is of course always necessary to have a reservoir of gas under high pressure so that it may be admitted through valve No. 1.

The window opening in the measuring chamber is two and one-half by one-half inch. The glass window itself is made of plate glass one-half inch thick sealed in place against the inside of the chamber with sealing wax. The sealing wax is painted over with Duco paint to prevent the dissolving of the sealing wax in the oil.

The procedure followed in making a set of measurements on the capillary rise with a given sample of oil and gas was as follows:

The capillary tube was cleaned thoroughly by allowing benzene to flow through it. The capillary tube was made easily removable by sealing it into a nut which screws into the end of the copper tube making connection to the capillary. The mixing chamber was filled with the proper quantity of oil and the apparatus made tight. The first measurement was taken at atmospheric pressure by leaving valves Nos. 2, 3, and 4 open and allowing the oil to run into the measuring chamber by opening valve No. 5. Enough oil is allowed to run into the chamber to just bring the meniscus in the capillary tube up to the marked position on the tube. The cathetometer is then set on the meniscus for the first reading, and the pointer is screwed down until it touches the surface of the liquid in the chamber. The oil is then forced back into the mixing chamber by closing valves 3 and 4, opening valve 5, and then gradually admitting gas through valve 1.

With the end of the pointer now clearly visible the cathetometer may be set on the point to get the second reading, and the height h is the difference between this and the first cathetometer reading. When all the oil is forced back into the mixing chamber valve 5 is closed and valve 3 is opened and gas allowed to flow in through valve 1 until the next desired pressure is reached as indicated by the pressure gauge. The stirrer is now put in operation and the oil and gas mixed until saturated. The saturation point is reached when the pressure read on the gauge ceases to drop, valve 1 being closed. Valves 3 and 5 are now opened and the saturated oil allowed to run into the measuring chamber for the second set of readings. This process is repeated again at the next higher saturation pressure and for the desired number of succeeding higher pressures.

Some trouble was experienced in keeping the meniscus stable in position.

Very slight currents of gas in the connecting tubing caused the meniscus to oscillate up and down. The difficulty was eliminated by making a very small hole in the tubing which connects to the capillary tube inside the measuring chamber. The hole was located just above the top of the capillary tube so that there was definite connection between the gas just above the meniscus and the gas in the surrounding chamber thus eliminating the possibility of a pressure gradient between these two bodies of gas. The resistance to flow of gas through the hole, however, was large enough so that it was easily possible

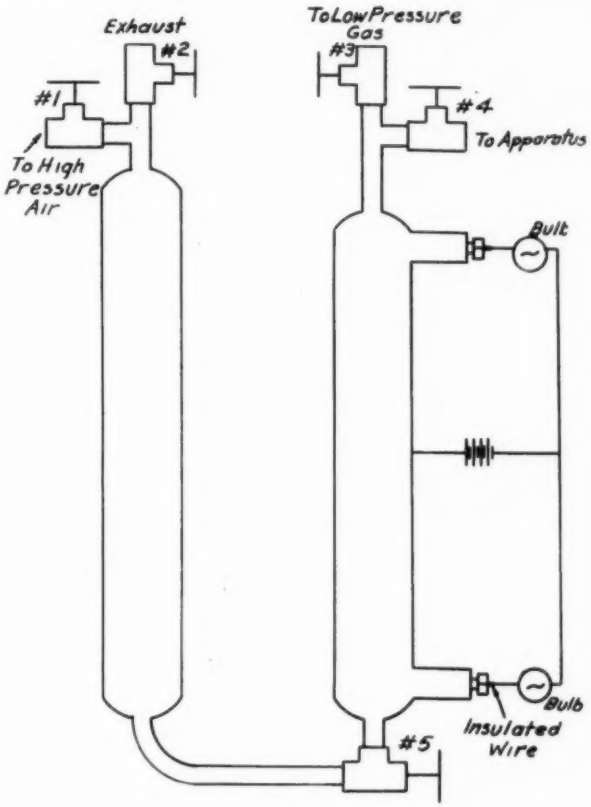

Fig. 2. Diagram of apparatus for compressing gas.

to expel the liquid from the capillary between measurements as explained above.

It was very desirable that the inside of the capillary tube be thoroughly wet near the meniscus to make sure that the final rest position was one of true equilibrium. This was accomplished by causing the liquid to rise too high in the tube and allowing it to slowly settle back into equilibrium. This excessive rise was easily brought about by suddenly opening and closing valve 4 (valves 2 and 3 being open) thus allowing a small amount of gas to rush out and set up currents in the connecting tubing which cause the meniscus to rise.

The entire apparatus was enclosed in an air-thermostated box so that the temperature variation in the apparatus could not exceed a small fraction of a degree. The constant temperature used was 31°C (88°F).

Since the gases used in this work were available only at the relatively low pressures of from 250 to 900 pounds it was necessary to construct an apparatus for compressing this gas up to the necessary high pressure. A diagram of this apparatus is shown in Fig. 2. It consists of two cylinders containing mercury which are connected at their bottom ends by a small pipe. The low

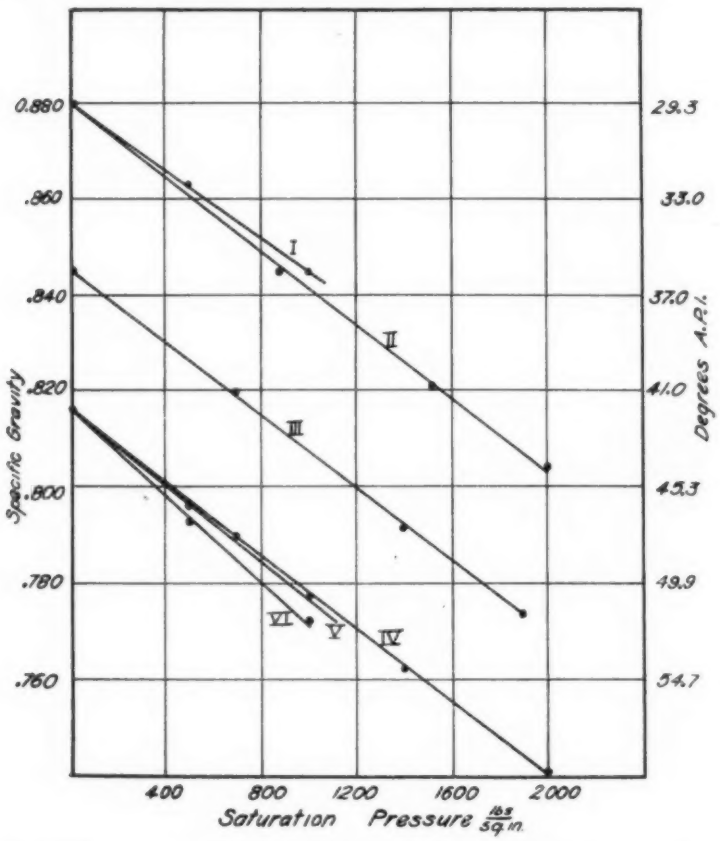

Fig. 3. Specific gravity of oil as a function of saturation pressure for various oil-gas combinations. I: Sugarland, Texas, crude oil; Santa Fe Springs, California, gas. II: Sugarland, Texas, crude oil; Sugarland, Texas, gas. III: Santa Fe Springs, California, crude oil; Sugarland, Texas, gas. IV: Lima, Ohio, crude oil; Sugarland, Texas, gas. V: Salt Creek, Wyoming, crude oil; Santa Fe Springs, California, gas. VI: Salt Creek, Wyoming, crude oil; Bartlesville, Oklahoma, gas.

pressure gas is admitted into the right hand cylinder through valve 3 thus forcing the mercury over into the left hand cylinder with valve 2 open. Valves 2 and 3 are now closed and valve 1 which connects to a tank of air at very high pressure is opened and the mercury forced back into the right hand cylinder compressing the gas therein which may be released into the main ap-

paratus through valve 4. This process may be repeated until the maximum pressure is reached.

The tank of high pressure air which furnishes the motive power was obtained from the liquid air plant compresser at about 3500 pounds pressure. Valve 5 was used for controlling accurately the flow of the mercury from one cylinder to the other. The level of the mercury in the right hand cylinder was indicated at its extreme positions by the flash light bulbs connected as shown to insulated wires leading into the cylinder which could make contact with the mercury on the inside.

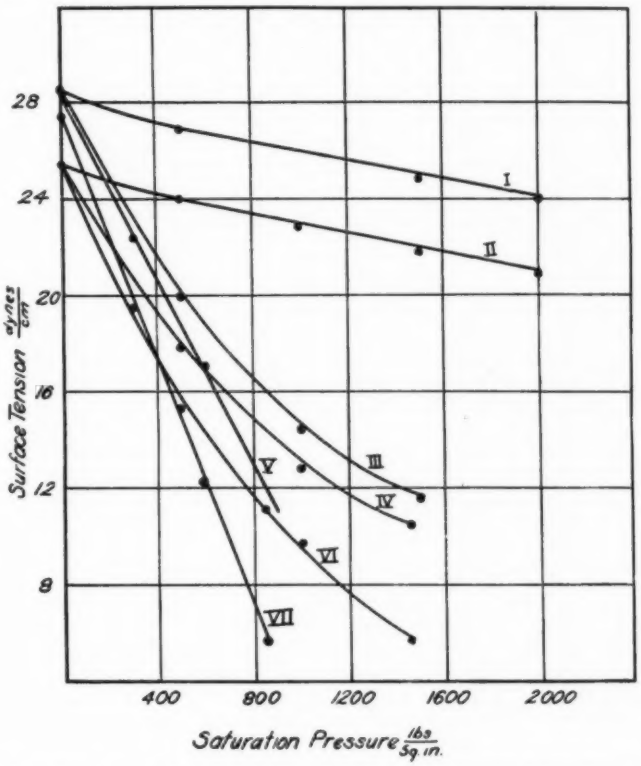

Fig. 4. Surface tension of oil as a function of saturation pressure for various oil-gas combinations. I: Sugarland, Texas, crude oil; air. II: Salt Creek, Wyoming, crude oil; air. III: Sugarland, Texas, crude oil; Santa Fe Springs, California, gas. IV: Salt Creek, Wyoming, crude oil; Santa Fe Springs, California, gas. V: Sugarland, Texas, crude oil; carbon dioxide. VI: Salt Creek, Wyoming, crude oil; Bartlesville, Oklahoma, gas. VII: Benzene; carbon dioxide.

Results

The natural oils and gases used in these measurements were chosen from various oil fields throughout the country. Natural gases from Sugarland, Texas; Seal Beach, California; and Bartlesville, Oklahoma were used as well as carbon dioxide and air. Crude petroleum from the Sugarland, Texas; Salt Creek, Wyoming; Sante Fe Springs, California; and Lima, Ohio, fields, as well as pure benzene were used as liquids. The results of the experiments are shown in the graphs of Figs. 3, 4, and 5.

Fig. 3 shows how the density varies with the saturation pressure for the various combinations of gas and oil used It will be noted that no curves are shown for air or carbon dioxide. This is because the variation in density with these gases was so small as to be less than the experimental error known to exist in other parts of the experiment. For all combinations shown, however, it is seen that the variation with pressure is practically linear and of approximately the same amount.

Figs. 4 and 5 show the variation in the actual surface tension with pressure of saturation. With air the decrease is very slow while with carbon

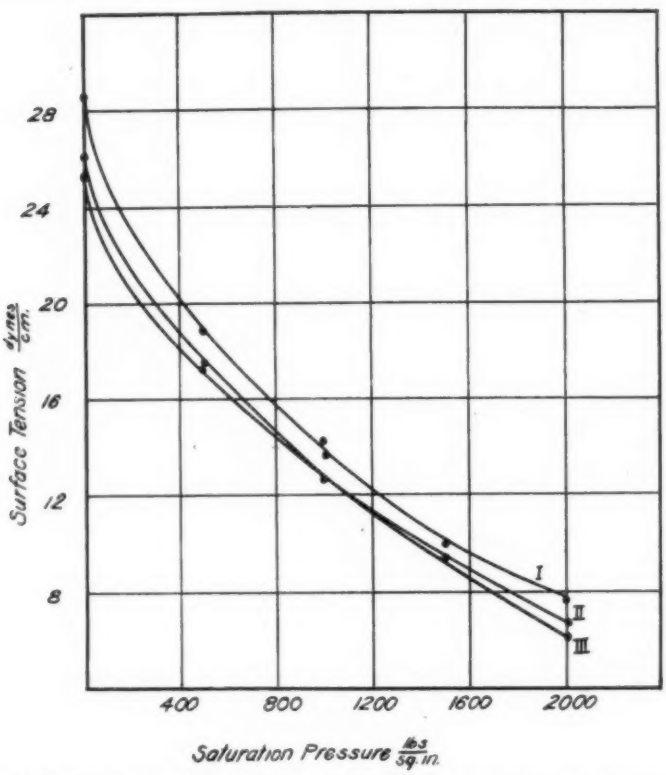

Fig. 5. Surface tension of oil as a function of saturation pressure of one gas in several oils. I: Sugarland, Texas, crude oil; Sugarland, Texas, gas. II: Lima, Ohio, crude Oil; Sugarland, Texas, gas. III: Santa Fe Springs, California, crude oil; Sugarland, Texas, gas.

dioxide it is very rapid, more rapid than with any of the natural gases used. With all gases except carbon dioxide the curves are slightly concave upward. In the case of carbon dioxide the curves are almost straight lines. This may be explained by the fact that carbon dioxide is the only pure gas used and in all other cases there may have occurred selective absorption of the various constituents of the gases or perhaps even successive condensation of some of the constituents. It is interesting that the curves for all the natural gases are of the same general shape and the relative decrease in surface tension of approximately the same amount.

No analysis has been made as yet for the sample of natural gas from Sugarland, Texas. The sample from Seal Beach showed the following fractionation analysis

Methane	87.83%
Ethane	4.52
Propane	3.61
Isobutane	0.62
n-butane	1.26
Isopentane and higher	2.16

The sample of natural gas from Bartlesville, Oklahoma, was furnished through the courtesy of the U. S. Bureau of Mines, Petroleum Experiment Station, who also furnished the following fractionation analysis.

Carbon dioxide	1.80%
Oxygen	0.48
Methane	75.224
Ethane	6.95
Propane	3.84
Butane plus	1.67
Nitrogen	10.04

The author wishes to thank Professor R. A. Millikan, under whose direction this work was done, for his interest and encouragement and also Professor W. N. Lacey for his interest and many valuable suggestions during the progress of the work. He is also indebted to the American Petroleum Institute for a grant which defrayed the expenses.

THE APPLICATION OF THE ULTRACENTRIFUGE TO SOME COLLOID-PHYSICAL PROBLEMS*

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(Received July 6, 1931)

UNTIL the past few years, methods for measuring particle size have generally been limited in applicability, rather inaccurate, and in general unsuited for determining the distribution of particle size. This has been especially true for the inorganic colloidal solutions in which particle size approaches molecular dimensions and for the important class of substances comprising the cellulose derivatives, gelatin and other proteins, synthetic resins, and rubber. In fact, most of our methods have been of an

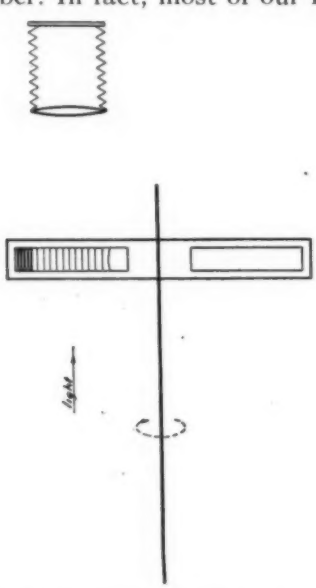

Fig. 1. Illustrating the principle of the ultracentrifuge.

indirect nature, as illustrated by the assumption that the change of viscosity during the treatment of cellulose nitrate or during the cooking of a synthetic resin reflects a change in the molecular or micellar sizes.

The development and the refinement of the ultracentrifuge by Svedberg and his associates[1] have provided a group of methods for determining particle size which promises to avoid many of the weaknesses of the earlier methods and to constitute the most reliable and adaptable technic for investigating dispersity in colloidal solutions.

* Communication No. 68 from the Experimental Station of E. I. du Pont de Nemours and Company.

[1] Svedberg, "Colloid Chemistry," 2nd ed., Chem. Catalog, New York, 1928.

The principle of the ultracentrifuge is illustrated in Figure 1. A transparent cell containing the solution or suspension to be studied is rotated at a speed sufficient to produce a centrifugal force 1,000 to 100,000 times that of gravity. A beam of light passes up through the cell and permits the colorimetric determination, either by visual examination or by photographic recording, of the changes undergone by the solution while the centrifuge is in action. If the solution contains equal-sized particles and the centrifuging is rapid enough, a sharp boundary moves outward. The particle size can then be determined by measuring the displacement of the boundary $x_2 - x_1$ in the time interval $t_2 - t_1$, and applying a modified form of Stokes' law. With nonuniform material, however, a partial separation is effected, giving one an opportunity to determine the distribution of sizes present from an analysis of the radial variation in concentration.[2]

From the molecular-kinetic standpoint there is no distinction between a colloidal particle and a molecule in solution.[3] The kinetic energy of any suspended unit which retains its identity is the same as that of a molecule, namely $3RT/2N$, where R is the gas constant, T is the absolute temperature, and N the number of molecules per mole; therefore, we shall use the term *micellar weight* as a generic name for the weight both of a suspended particle and of a molecule in solution. *Particle size* will be used to designate the equivalent radius of the molecule or particle.

In a sedimenting system of molecules or very small particles, diffusion produces a blurring of the boundary that cannot be neglected. The basic differential equation which expresses the sedimentation and diffusion relations of a system of small particles in a centrifugal field of force[4] is

$$\frac{dc}{dt} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{1}{x}\frac{\partial c}{\partial x}\right) - \omega^2 x s\left(\frac{\partial c}{\partial x} + \frac{2c}{x}\right) \tag{1}$$

where D is the diffusion constant and s is the sedimentation velocity per dyne. In a uniform field (as of gravity) the second and fourth terms drop out, leaving the ordinary differential equation for the combined action of diffusion and sedimentation on a system of small particles, which has been treated by Mason and Weaver.[5] The thermodynamic relations are expressed by the following equation:[6]

$$dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial p}\right)dp + \left(\frac{\partial F}{\partial c}\right)dc \tag{2}$$

which describes the change in free energy as a function of distance from the center, hydrostatic pressure, and concentration.

[2] Svedberg and Rinde, J. Am. Chem. Soc. **46,** 2677 (1924).

[3] Einstein, Ann. d. Physik (4) **17,** 549 (1905).

[4] Lamm, Arkiv Mat., Astro. Fysik **21B,** No. 2 (1929); Lamm, Zeits. f. physik. Chem. **143A** 177 (1929).

[5] Mason and Weaver, Phys. Rev. (2) **23,** 412 (1924).

[6] Lewis and Randall, "Thermodynamics" McGraw-Hill, New York, 1923, page 244; Svedberg and Nichols, J. Am. Chem. Soc. **48,** 3081 (1926).

If we start with an initially uniform concentration of particles (Figure 2) the first stage, t_1, is that in which there is still no clear liquid at the meniscus. As the sedimentation proceeds the particles leave the meniscus region, and if the cell is long enough, there is still a region of uniform concentration below the boundary region (t_2). This is the simplest case because here we can consider the column of solution as of infinite extent and can readily determine both the sedimentation velocity and the diffusion constant.[7] When the sedimentation has progressed somewhat further, t_3, the advancing wave of particles diffusing from the bottom reaches the boundary region, and the mathematical analysis becomes rather complicated. Finally, after a much longer time, t_4, an equilibrium is established between the diffusion of the

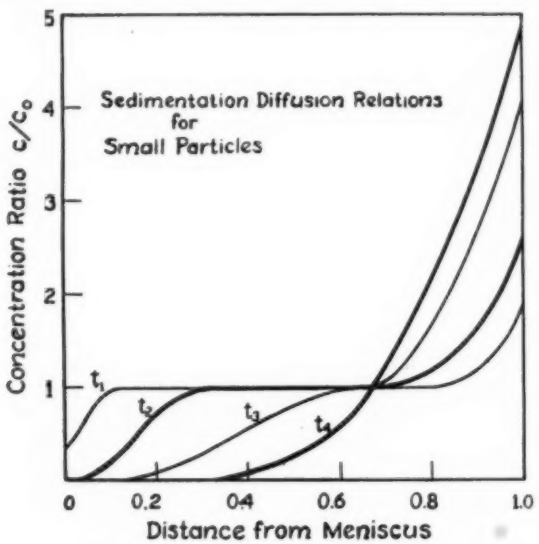

Fig. 2. Schematic representation of the variation of concentration with time during the establishment of a sedimentation equilibrium in the ultracentrifuge. Mason and Weaver (loc. cit.) give exact curves for a gravitational field.

particles and the sedimentation. Thus, depending on the experimental conditions, size of particle may be determined from observations either of the sedimentation velocity, diffusion, or sedimentation equilibrium.

At sedimentation equilibrium the change in free energy, dF, or the change in concentration with time, dc/dt, becomes equal to zero at every point; integration gives the following relations for the sedimentation equilibrium:

$$M = \frac{2RT\, ln\, (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \tag{3}$$

or

$$r = \left[\frac{3RT\, ln\, (c_2/c_1)}{2N\pi(\rho_p - \rho_m)\omega^2(x_2^2 - x_1^2)}\right]^{1/3} \tag{3a}$$

[7] Svedberg and Nichols, J. Am. Chem. Soc. **49**, 2920 (1927).

where M is the micellar weight, r the effective radius of the particle considered as a sphere, R the gas constant, 83.2×10^6, T the absolute temperature, N the Avogadro number, V the partial specific volume of the substance, ρ the density of the solution, ρ_p the density of the particle, ρ_m the density of the solvent, ω the angular velocity, and c_2 and c_1 the concentrations at the points x_2 and x_1 distant from the axis of rotation of the centrifuge. Inspection of equation (3) shows that no assumptions have been made as to form and structure of the molecule or particle. In addition, there are no membrane complications as in the osmotic-pressure method of determining micellar weight, and the presence of electrolytes is beneficial rather than harmful in that electrical potentials due to the separation of electrical charges having different mobilities are repressed.

For case t_2, shown in Figure 2, in which the liquid can be considered of infinite extent, fulfillment of the condition that the centrifugal force per mole is equal to the frictional force per mole leads to the simple sedimentation-velocity equations for small x-intervals:

$$M = \frac{RTs}{(1 - V\rho)D} \tag{4}$$

or

$$r = \left[\frac{9\eta s}{2(\rho_p - \rho_m)}\right]^{1/2}. \tag{4a}$$

For the first equation the frictional coefficient f is evaluated from the Einstein diffusion equation: $f = RT/D$. Both D, the diffusion constant, and s, the sedimentation constant $(=(1/\omega^2x)\cdot(dx/dt)$, characteristic of each molecular species or particle-size, are calculated directly from the data obtained during the centrifuging.[8] For the second equation the frictional constant is evaluated as is customary from Stokes' law.

A centrifuge developing a centrifugal force of 1,000–10,000 times that of gravity enables us to study the sedimentation velocities of the lyophobic inorganic colloids and the sedimentation equilibria of the proteins and other organic lyophilic substances of micellar weight greater than 10,000. For the determination of the sedimentation velocities of lyophilic substances of micellar weight greater than 15,000 and for the sedimentation equilibria of most substances in the micellar range 10,000–1,000, centrifugal forces of about 100,000 times that of gravity are required.

The most important conditions for satisfactory ultracentrifugal analysis are: First, no vibrational or thermal effects should disturb the sedimenting system; second, the amplitude of vibration of the rotor must be small enough and the optical system well enough defined that sharp pictures can be obtained; third, cells should be well enough constructed to withstand pressures of 100 to 200 atmospheres produced when the centrifugal force reaches the magnitude of 100,000 times that of gravity; fourth, the substance must undergo no deterioration during the centrifuging.

[8] Svedberg and Nichols, J. Am. Chem. Soc. **49**, 2920 (1927).

An improved form of ultracentrifuge used at the du Pont Experimental Station will serve as an example of the machines developed for investigations requiring moderate centrifugal forces.[9] This machine was constructed to enable us to use either a colorimetric or a refractive-index method for measuring concentration changes. In some systems, for example rubber in benzene, cellulose nitrate in acetone, or cellulose in cuprammonium solution, the light-absorption method is not applicable because both the solvent and the dissolved substance absorb light in the same region and the spectrum. However, if the solution is not turbid, the index-of-refraction method is more generally applicable because the refractive index of the solute is rarely identical with that of the solvent The method depends simply on the measurement of the displacement of the lines of a micrometer scale photographed through the solution in the centrifuge cell.[10]

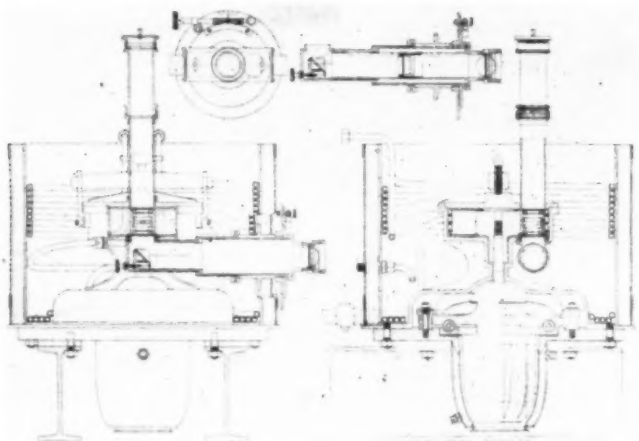

Fig. 3. Improved form of ultracentrifuge.

In order to increase the sensitivity of the method and to insure freedom from parallax, a photographic lens of rather long focal length is used, i.e., about a meter and a half. The centrifuge itself is shown in cross section in Figure 3. It is built on the base of a rayon-spinning centrifuge designed by Siemens and Shuckert.[11] Any tendency to injurious vibration is immediately counteracted by a rubber ring on which a wide flange of the synchronous motor rests. The speed is regulated by means of a frequency transformer which renders possible a variation in speed from about 1500 to 12,000 r.p.m. Exposures are made by means of electromagnetically operated shutters. Speed is indicated by means of a magneto connected to the frequency transformer. As in the earlier types of centrifuges, we have thermostatic control

[9] Cf. Svedberg and Sjögren, J. Am. Chem. Soc. **51,** 3594 (1929). Earlier types have been described by Svedberg and Nichols, J. Am. Chem. Soc. **45,** 2910 (1923); Svedberg and Rinde, reference 2; and Svedberg and Heyroth, J. Am. Chem. Soc. **51,** 550 (1929).

[10] Lamm, Zeits. f. physik. Chem. **138A** 313 (1928); **143A,** 177 (1929).

[11] Elsässer, Siemens Zeits. **12,** 580 (1925).

from 0 to 50 or 60°C, and hydrogen or helium is blown through the rotor chamber to cut down frictional heat.

For some purposes, however, it is desirable to have available extremely high centrifugal forces of the order of 100,000 times that of gravity. Then it is possible to determine the sedimentation velocity of lyophilic substances in

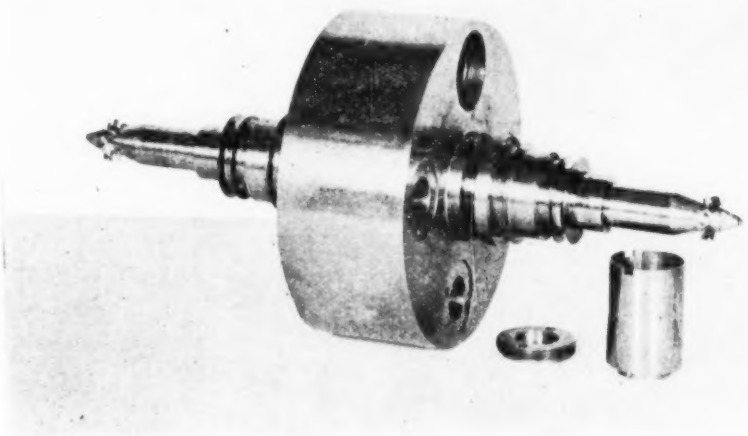

Fig. 4. Rotor of oil-turbine type of ultracentrifuge.

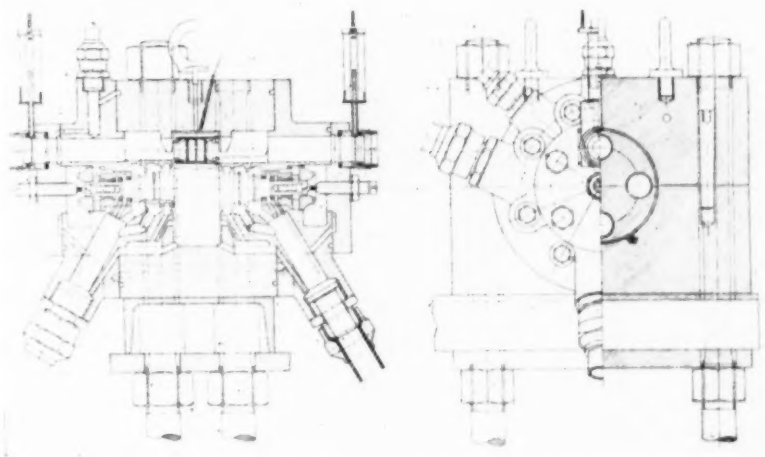

Fig. 5. Diagrammatic representation of the oil-turbine type of ultracentrifuge.

two or three hours which might require from two to three days to attain sedimentation equilibrium with a low speed. If we are working with unstable materials that change continuously, this is a very decided advantage. It is also possible to obtain more exact information on mixtures of molecules because of the greater separation in the higher centrifugal field.

The oil-turbine type of ultracentrifuge was developed by Svedberg and Lysholm[12] to produce fields of force up to 100,000 times that of gravity and yet not heat injuriously. Figure 4 shows the rotor. Figure 5 gives a diagrammatic representation of the centrifuge. The rotor is made of chrome-nickel steel and has openings for four cells. It is driven by oil under a pressure of twelve atmospheres impinging against two eight-bladed turbines, one at each end of the shaft. The rotor revolves in hydrogen or helium gas at a reduced pressure. Under optimum conditions the temperature difference between the rotor and the casing is only 1.5 degrees at 40,000 r.p.m. The oil from the

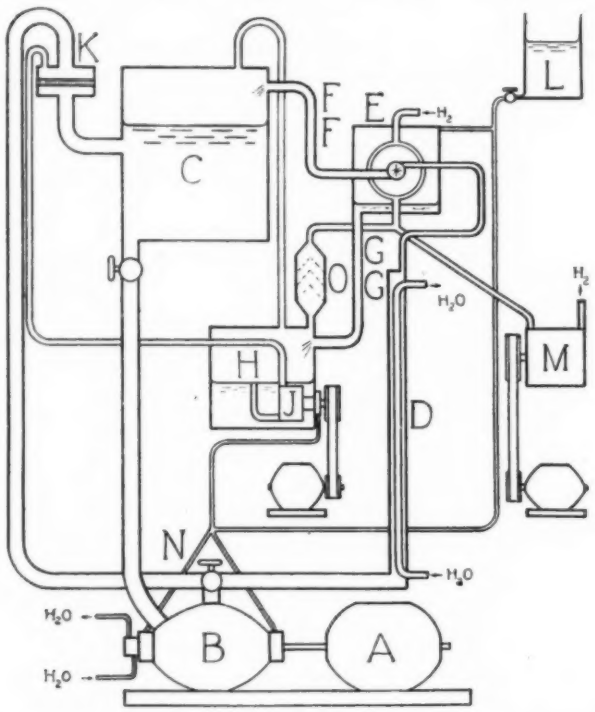

Fig. 6. Oil and hydrogen circulation system of the oil-turbine type of ultracentrifuge.

bearings is prevented from entering the rotor chamber by an elaborate system of deflectors. The temperature is adjusted by cooling the oil before it is admitted to the turbine chambers. The observation windows are protected from oil mist by electromagnetically controlled shutters. The speed of the rotor is determined by means of a stroboscopic tachometer.

The complete oil and hydrogen circulation system is shown in Figure 6. The oil is pumped from the large oil container (*C*) through the oil cooler (*D*) to the centrifuge and then back to the oil container. Part of the oil, however, lubricates the bearings and drains down into the lower container (*H*) from which it is pumped through the filter (*K*) to the main container.

[12] Svedberg and Lysholm, Nova Acta Reg. Soc. Scient. Upsaliensis. Vol. ex. ord. ed. (1927); Svedberg and Nichols, J. Am. Chem. Soc. **49**, 2920 (1927).

Applications

The following figures will give some idea of the range of problems to which the ultracentrifuge has been applied.[13]

Figure 7 gives a photographic reproduction of a sedimentation equilibrium of a 1.9% solution of egg albumin subjected to a mean centrifugal force about 5800 times that of gravity at 17°. The series from left to right shows the exposure at the start of the centrifuging followed by 40-second

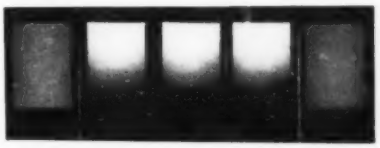

Fig. 7. Sedimentation equilibrium of egg albumin.

exposures after 39.5, 45.5, and 51 hours of centrifuging respectively. Evidently complete equilibrium was reached in less than 40 hours. The last exposure to the right was taken after the solution was remixed at the end of the experiment. As an example of the sedimentation-velocity method Fig. 8 gives a reproduction of the photographic record of the centrifuging of a 1% solution of carbon monoxide-hemoglobin subjected to a field of force

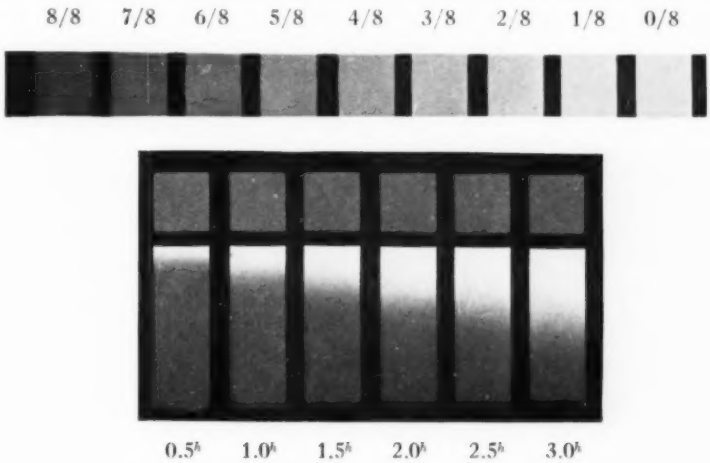

Fig. 8. Sedimenting carbon monoxide-hemoglobin.

87,000 times that of gravity. It shows the sedimentation of the solution 0.5, 1 · · · 3 hours after the start of the run. The top row is the scale of concentrations in fractions of 1%.

By means of the ultracentrifuge it has been demonstrated that many proteins exist as single molecular species. Figure 9 gives the variation of concentration with distance after 0.5, 1.0 · · · 3 hours of centrifuging of carbon

[13] Cf. Nichols, Sixth Colloid Symposium, 1928, p. 297 et seq.

monoxide-hemoglobin, a photographic record of which was given in the previous figure.[14] The dotted curves for two and three hours represent the theoretical diffusion curves for a substance with a uniform molecular weight of 68,000 subjected to the same experimental conditions.

When charged particles or ionized molecules are present in a solution, centrifuging produces a partial separation of charges, thus introducing an electrical potential acting in opposition to the centrifugal potential. How-

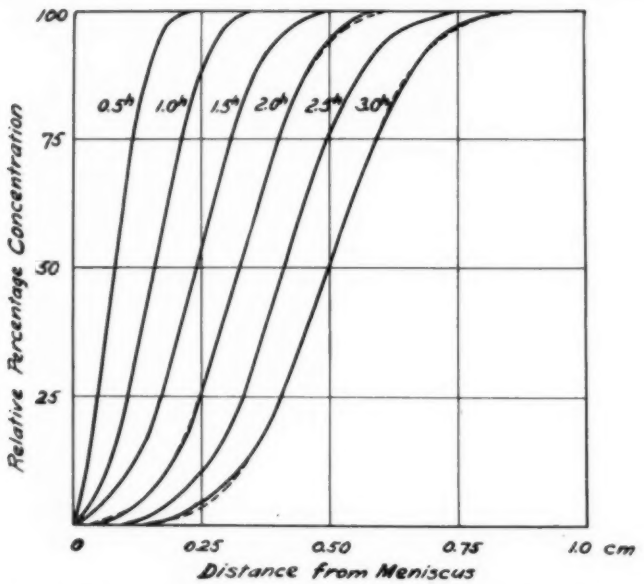

Fig. 9. Concentration curves of carbon monoxide-hemoglobin.

ever, if sufficient electrolyte is added to the solution this electrical potential can be almost totally repressed. Tables I and II are given to illustrate this phenomenon. In addition, they show that it is possible to determine centrif-

TABLE I. *Sedimentation equilibrium of 0.5% sodium eosinate.*

Speed 11,700 r.p.m. ($\omega = 390\pi$); mean centrifugal force $= 8.65 \times 10^6$ dynes; $T = 305°$; Eastman Process plates; parallel light—no filter; length of column 0.50 cm; exposure times 40 min.

Hours from start	Distances, cm x_2	x_1	Mean concentration c_2	c_1	M
17.5	5.92	5.52	98.0%	95.2%	398
23.5	5.92	5.52	97.85	94.9	421
29	5.92	5.52	98.75	95.95	396
	5.92	5.52	98.95	96.15	395
				Ave.	403

Value for completely dissociated Na_2 (Na Eosinate)$_2 = 446$
Molecular weight from boiling point elevation:
2% solution, $M = 530$
2.5% solution, $M = 601$

[14] Svedberg and Nichols, J. Am. Chem. Soc. **49**, 2920 (1927).

ugally the molecular weights of substances of small enough magnitude to give fairly reliable results by the ordinary methods of physical chemistry. A 0.5% salt-free solution of eosin dye was subjected to a centrifugal force 9,000 times that of gravity, and the value 400 was obtained for the apparent molecular weight. This is of the same order as that obtained by the ordinary boiling-point method, 530 and 601. The ionization of the dye of course affects both methods; however, the opposing electrical potential arising in the centrifuge from the partial separation of the large dye ions from the small sodium ions may be repressed by the addition of 1% sodium chloride. Under these conditions, the dye was found to consist in solution of molecules twice the formula weight, as shown in Table II.

TABLE II. *Sedimentation equilibrium of 0.5% sodium eosinate in 1% sodium chloride solution.*

Speed = 11,700 r.p.m.; ($\omega = 390\pi$); mean centrifugal force = 8.65×10^6 dynes; $T = 303.5°$; Eastman Process plates; parallel light—no filter; length of column 0.44 cm; exposure times 30 min.; photographic records taken 13.5, 18, 24, and 36 hrs. after the start.

Distances, cm		Mean concentration			
x_2	x_1	c_2	c_1		M
5.92	5.87	103.93%	102.52%		1446
5.87	5.82	102.52	101.20		1385
5.82	5.77	101.20	100.06		1219
5.77	5.67	100.06	97.66		1324
				Ave.	1343

Molecular Weight of Na_2 (Na Eosinate)$_2$ = 1384
Ionic Weight of (Na Eosinate)$_2^{--}$ = 1338

A reproduction is given in Fig. 10 of the photometer record of a sedimentation equilibrium of another dye—erythrosine—at the start and after equilibrium has been reached. This is given to indicate that even with certain relatively small molecules an easily measurable effect takes place in the centrifuge.

Figure 11 shows the distribution curves of a graded series of gold sols prepared by successive depositions of gold on the particles of a nuclear gold sol containing practically the smallest particles that can exist without resolution in the medium. This series was used by our x-ray laboratory in their analysis of the methods for determining particle size by the broadening of the x-ray diffraction patterns.

Figure 12 shows that the distribution curves of a positively and a negatively charged ferric oxide sol may be very similar. The negative sol was obtained from the original, positively charged sol by adding sufficient potassium citrate to discharge it and restabilize it with negative citrate ions. The mean radii are nearly the same, 3.85 millimicrons for the original sol as compared with 4.2 for the reversed sol. It seems likely that identical distribution curves can be obtained under properly controlled conditions. This signifies that we are dealing with a system of primary particles.

It should be mentioned that the distribution curves given in the last two figures were based on the light transmitted by the colloid in the centrifuge

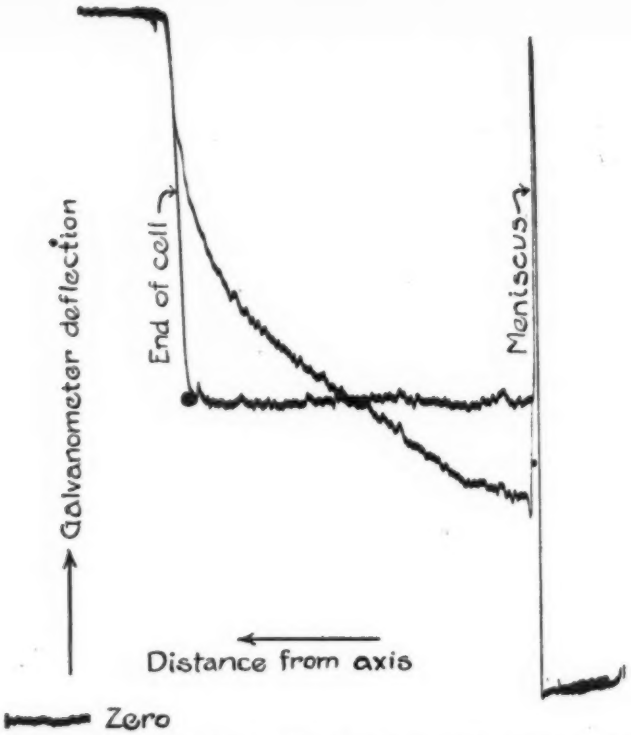

Fig. 10. Photometer record of the centrifuging of erythrosine. Horizontal line, initial condition; sloping line, after equilibrium.

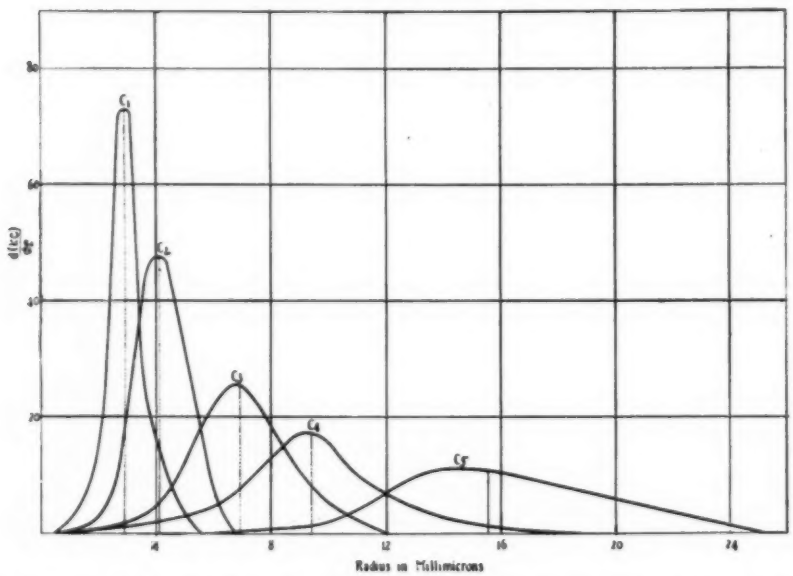

Fig. 11. Weight-optical distribution curves of a graded series of gold sols prepared by the nuclear method.

Sol	Mean radius	Area
c_1	2.9 mμ	108%
c_2	4.1	114
c_3	6.9	106
c_4	9.4	96
c_5	15.6	102

and therefore contain implicitly the variation of light absorption with particle radius. If the particles of the substance are fairly uniform in size, or if the light absorption is nearly constant over a range of sizes, then these distribution curves, which we may call *weight-optical* curves, coincide with the *weight-distribution* curves. Usually these conditions are not fulfilled. Then it is necessary to know the relationship between particle size and the light absorption or other property in question. The approximate relation may be determined as follows. First, the weight-optical distribution curves are obtained for a series of fractions of the colloid containing somewhat different ranges of particle sizes. Next the distribution curves are divided into size-

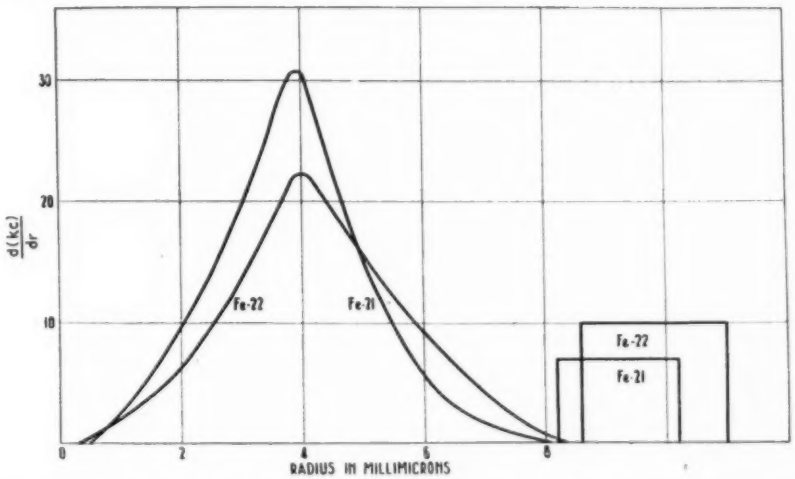

Fig. 12. Comparison of the weight-optical distribution curves of ferric oxide before and after reversing the charge with potassium citrate.

Sol.	Treatment	Primary mean radius	Primary area	Secondary mean radius	Secondary area
(Fe-21)	None	3.8 mμ	84%	ca. 20 mμ	14%
(Fe-22)	Charge reversed with 0.1 *M* K_3 citrate	4.2	76	ca. 20	24

classes and a series of simultaneous equations formed containing the optical concentration (product of the actual concentration by the unknown absorption coefficient of the size-class) of the material present in each size-class. This system of equations is solved for the unknown light absorption coefficients. With the use of these absorption coefficients the weight-optical distribution curves determined in the ultracentrifuge may be converted to weight-distribution curves independent of the variation of light absorption with particle size. Similarly, if we determine the average light-scattering powers for the series of fractions with a turbidimeter or nephelometer the above procedure can be used to determine the variation of light-scattering power with particle size.

Table III summarizes the regularities obtained by Svedberg and his co-workers[15] in the molecular weights of proteins and other complex substances. It will be noticed that the micellar weights of the monodisperse, native proteins, with the exception of the hemocyanins, fall into classes of one, two, three, and six times 34,500. This rather surprising regularity and others found

TABLE III. *Micellar weights of naturally occurring substances (Svedberg and co-workers)*

Substance		Micellar weight	Approximate multiple
Monodisperse proteins			
Class I	Egg albumin, insulin, and Bence-Jones' protein	34,500	1×34,500
Class II	Hemoglobin and serum albumin	68,000	2×34,500
Class III	Serum globulin	104,000	3×34,500
Class IV	Edestin and 7 plant globulins	208,000	6×34,500
Class V	Hemocyanins	$2\text{–}5\times10^6$	
Polydisperse proteins			
	Casein, lactalbumin, gelatin, muscle globulin, and ten others.	Mean micellar weight falls in approx. same range as monodisperse proteins.	
Cellulose			
	Cotton linters	40,000	
	Wood	40,000 and smaller	
	Viscose (cellulose xanthate)	33,000 (approx.)	

by Svedberg[16] remained without explanation until some recent considerations put forth by Astbury and Woods.[17] They suggest that the sequence of numbers: 1, 2, 3, and 6 may arise from the crystallographic configurations that neighboring peptid chains can assume when linked together by the secondary valences of –CO– and –NH– groups. Such molecular associations might be expected to be reversible, an assumption verified by the experimental findings of Svedberg and his associates.[18] Astbury and Woods attempt to explain the fundamental unit of weight by suggesting that the primary-valence chains are limited to a length corresponding to 34,500 owing to vibrational instability.

The determination of the micellar weight of different forms of cellulose in cuprammonium solution was carried out by Stamm.[19] He found cotton linters alpha-cellulose to be monodisperse and to have a micellar weight of 40,000 on a copper-free basis. The wood celluloses contained material of micellar weight 40,000 and 20,000 and degradation products of much lower weight. The sample of viscose prepared from the same cotton linters alpha-cellulose had a somewhat lower micellar weight, approximately 33,000.

[15] Svedberg, "Colloid Chemistry," 2nd ed., Chem. Catalog, New York, 1928, page 164; Svedberg, Kolloid-Z. **51,** 10 (1930).

[16] Svedberg, Nature **123,** 871 (1929).

[17] Astbury and Woods, Nature **127,** 663 (1931).

[18] Cf. Svedberg and Sjögren, J. Am. Chem. Soc. **52,** 279 (1930).

[19] Stamm, J. Am. Chem. Soc. **52,** 3047, 3062 (1930).

By these examples, drawn from various investigations carried out in the past few years on the constitution of the proteins and other naturally occurring substances, on complex dyes, and on colloidal gold and ferric oxide, it is hoped to convey, in some measure, the breadth of the field of usefulness of the ultracentrifuge. In its continued development it promises to furnish the most powerful and the most generally applicable technic for investigating many molecular-kinetic problems.

THE APPLICATION OF PHYSICS IN CERAMICS

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THE ceramic arts which deal with the utilization of the nonmetallic minerals and rocks, while sometimes classified as chemical industries are such only in part. To a very large extent they are based on physical phenomena and the physical factors predominate.

From the operative standpoint, manipulative skill still determines the primary success of the processes involved. That this condition exists is due to the fact that these industries are not dealing with definite chemical entities but with rock products the properties of which are subject to the results of the geological processes which have evolved them. In their use, the physical properties must of necessity predominate. The final operation, that of firing the ceramic products, has for its object the production of artificial, igneous rock and deals with the interaction of solid particles, resulting at best, in systems of high viscosity in which the boundaries between the mineral grains are still well defined.

It might as well be realized that under such conditions chemical reactions are decidedly incomplete, and that the processes of solution and transformations in crystalline structure are of greater importance. It is only when we come into the field of the glasses that we find more homogeneous systems. While the gross chemical composition does enter into the problem, the chief effects with which we are concerned, are those of the resulting physical structure in the determination of which we must be guided by physical tests. Purely chemical methods of control do not exist as yet, just as the chemistry of the reactions between solids, at elevated temperatures, has so far been confined to the study of pure reagents under carefully controlled laboratory conditions.

Taking one of the basic raw materials of ceramics, the substance known as "clay," we find it to exist in nature in a multitude of forms, differing more widely physically than chemically. Its outstanding property is the physical one of plasticity. While the practical man has little difficulty in estimating this quality for his purposes by means of the tools of his trade, the experimenter finds it a hard task to evaluate plasticity in precise terms. Though some progress has been made in this direction through the work of Bingham, and others, this elusive property does not conform entirely to our present ideas of "plastic" flow. But it is evident that this problem can be approached only from the physical standpoint.

The measurement of the particle sizes of clays is obviously one of physical methods and we make use of separations which are based on Stokes' law, or employ optical principles. Again, the electrical charges carried by the fine particles give rise to various phenomena which are utilized as in the electro-

osmotic processes. Owing to the fineness of the particles the presence of small amounts of electrolytes may affect the consistency of clays in the suspended or plastic states considerably, and here it does seem that we are concerned with definite chemical effects. But in dealing with such conditions we must resort to physical measurements, consisting in the determination of density, relative fluidity or electrical resistance.

In this connection must be mentioned the importance of the petrographic microscope in the examination of pulverized, crystalline materials which carry such minerals as quartz, feldspar and mica.

The ceramist must also concern himself with the properties of the shrinkage of clays in drying, the porosity and the mechanical strength in the dry state. The latter property is frequently expressed by the modulus of rupture of molded bars and is of importance since high strength often lowers shop losses in a very decided manner. The drying process itself must be controlled by means of temperature and humidity measurements in order that conditions be provided which permit of safe drying. This involves also the determination of the air volumes and air velocities which cause the circulation in the drying chambers.

In the firing of ceramic products the measurement of the kiln or furnace temperatures is, of course, of prime importance and these are determined most frequently by means of thermocouples connected to direct reading millivolt meters or potentiometers. Optical pyrometers also find frequent application. The success of this operation depends on the skilful use of such instruments, especially in connection with the modern tunnel kilns. Of late, the application of automatic temperature control has made considerable progress. Of no less importance is the measurement of the slight plus or minus pressures which prevail in different sections of continuous kilns and which require careful control.

The application of glazes and enamels to once fired or raw ware offers perplexing problems dealing with the density and fluidity of the aqueous suspensions which are used. Too fluid or too viscous glazes cause real difficulties in their application which can be overcome only through patient study of the physical and chemical factors involved. No less difficult is the proper fitting of the glazes to the body of the product from the standpoint of the thermal expansion of the two materials. Cracking or peeling of the fused glaze will take place unless the two expansions are in satisfactory agreement. This makes it desirable to know the thermal expansion of both the glassy coating and the clay body. Considerable attention is being paid to this subject at the present time and the apparatus used may vary from the comparison of the expansion of the specimen with that of a quartz glass tube in an electrically heated furnace, by means of micrometer microscopes or sensitive gauges, to the wave-length method of Fizeau. In industrial plants the coefficient of thermal expansion is frequently computed from constants determined for the various oxides which make up the glaze mixtures, by several investigators.

Aside from the thermal expansion we must deal also with the changes in volume to which the more porous ceramic products are subject in use or

storage, when they are saturated with water vapor. While this expansion is exceedingly slight and is of no importance in connection with unglazed products, it is apt to set up stresses in any glazes that may be applied. Although it is possible to counteract such stresses by appropriate heat treatment it is desirable to be informed concerning the magnitude of this expansion which is in part reversible.

Formerly, the physical properties of finished ceramic products have been taken for granted but at the present time there is not only a demand for information concerning such qualities as the mechanical strength under compressive, tensile and transverse stresses, hardness, resistance to impact, thermal expansion, resistance to thermal shock, dielectric strength, electrical resistance at higher temperatures, porosity, weather resistance, etc., but more and more, definite specifications are being prepared by the purchasing public. In certain fields, such as the refractories used in furnace construction, very comprehensive classifications and requirements have been established.

This trend has resulted not only in a more extensive application of physical tests but has also aroused interest in the study of the microstructure as well as of the ultimate structure of ceramic products. For this reason not only is greater use being made of petrographic work but x-ray analysis has also been introduced.

The expansion of the work in physical measurements indicates a healthy development of the ceramic industries which is certain to increase their usefulness and strength.

THE EDITOR'S COLUMN

The Quantum Theory of the Metallic State

IT IS only within the last five or six years that the theoretical physicist has been in possession of methods powerful enough to allow him to cope with the problem of the metallic state. With the quantum mechanics to aid him, he has made definite progress but even so only the preliminary steps have been taken. A rough survey of the territory has been made and certain guide-posts have been erected, but the field is still open to the adventurous physicist who is not deterred by difficulties.

It is fairly clear that the general picture of a metal may be taken as that of a crystal in which the atoms are so closely spaced that a sort of mutual ionization process occurs which permits one or more of the valence electrons to pass from atom to atom. Presumably all stages of freedom for the valence electrons may be possible depending upon the ionization potentials of the atoms, the lattice spacing, the temperature, etc. so that under some circumstances, the electrons may be rather tightly bound to the atoms while under others they can move about in the lattice practically without hindrance. The mathematical theory has been developed in great detail only for cases in which the conduction electrons can be considered entirely free from the atoms and play the role of an "electron gas." This conception is in itself not new, but was used by Lorentz and Drude, years ago to give a theoretical interpretation of the Wiedemann-Franz law, but it was later more or less abandoned because it gave much too large a value for the specific heats of metals.[1] Pauli,[2] and more especially Sommerfeld[3] observed that the difficulty with the theory lay not so much in the physical conception behind it as in the assumption that the electron gas acts like an ordinary gas and obeys the Maxwell-Boltzmann distribution law. Instead, they pointed out that the actual distribution ought to be that of Fermi as derived from the statistical theory developed by Fermi and later also by Dirac. This substitution of the Fermi-Dirac statistics for that of Maxwell-Boltzmann actually did do the trick, and the theory of metals which was developed by Sommerfeld in 1928 has now become one of the standard tools in the study of thermionic emission, photoelectric effect, Hall effect, etc.[3a]

In the meantime the quantum mechanical theory was being developed from another angle. Starting from the idea that the electrons were bound to the atoms instead of wandering more or less freely throughout the metal, Heisenberg[4] attacked the difficult problem of constructing a theory of ferromagnetism. His two principal aids were the electron "spin" and the "exchange effect." The first of these notions is quite simple and has been discussed in these columns previously.[5] The second is more sophisticated and can be properly understood only in connection with the mathematical theory of quantum mechanics. Its basis lies in the fact that since all electrons are exactly alike we cannot tell the difference if two of them be interchanged, and so must allow for such an "exchange" of any two electrons at any instant. When this possibility is put into the mathematical theory it is found that it has a profound effect in de-

[1] cf. K. K. Darrow, "Statistical Theories of Matter, Radiation, and Electricity," Rev. of Mod. Phys. **1,** 90 (1929) for a more detailed account of this subject, and especially Sommerfeld's theory.

[2] W. Pauli, Zeits. f. Physik **41,** 81 (1927).

[3] A. Sommerfeld, Zeits. f. Physik **47,** 1 and 43 (1928).

[3a] cf. S. Dushman, "Thermionic Emission" Rev. Mod. Phys. **2,** 381 (1930) A. Sommerfeld and N. H. Frank, "Statistical Theory of Thermoelectric, Galvano- and Thermomagnetic Phenomena in Metals" Rev. of Mod. Phys. **3,** 1 (1931).

[4] W. Heisenberg, Zeits. f. Physik **49,** 619 (1928). cf. also L. W. McKeehan, "Magnetism in Discontinuous Media." Rev. Mod. Phys. **2,** 477 (1930).

[5] Physics **1,** 69 (1931); **1,** 139 (1931).

termining the way in which two atoms interact with each other. There is nothing mysterious about this "exchange effect," but one should refrain from worrying about its significance until after he has examined the mathematical theory. On the foundation of these two conceptions, Heisenberg was able to give some account of the meaning of ferromagnetism, although even so some further assumptions about the magnitudes of the exchange effect were necessary in order to arrive at quantitative results.

IMPORTANT extensions of the theory were soon made by Bloch[6] and Slater[7] whose work shows particularly well how the transition from the electron gas theory of Sommerfeld to the bound electron theory of Heisenberg is to be made, thus opening the way to a more complete theory of actual metals which undoubtedly have properties intermediate between the extreme cases considered by Sommerfeld and Heisenberg. Bloch gave a wave-mechanical method of describing the motion of an electron progressing through the crystal but having occasional encounters with the atoms, so that it sometimes gets turned around or scattered in another direction. This description of the electronic motion is very well adapted to a discussion of topics related to the conduction of electricity and heat by metals since it deals directly with the passage of the electrons through the lattice; it has also been applied by Kronig[8] with some success to the theory of the reflection of light in the ultraviolet region of the spectrum. Slater, on the other hand, prefers to treat a metallic crystal like a super-molecule, determining the energy levels of this gigantic quantum dynamical system approximately from the states of the individual atoms. He has treated specifically only monovalent metals, so that one need worry only about a single outer electron for each atom, but instead of assigning only one valence electron to an atom at a time, as was done by Heisenberg, Slater assumes that there can be at most two electrons on an atom at a time, some of the atoms being ionized for a part of the time. In general, for atoms with a more complicated outer structure one would have to allow for states in which more than one extra electron could crowd on a given atom, but these results do not differ in principle from those found by Slater. The picture of conduction which is offered by this theory is very interesting at ordinary temperatures most of the atoms have one valence electron attached to them, but a few will have two electrons and a corresponding number will be ionized. Under the influence of the external field an electron can easily pass from an atom onto an adjacent ion, and an atom which has two electrons can easily lose one to another atom or ion. One can thus think that *two* kinds of conduction are in operation, one by the bound electrons which leave their own atoms to attach themselves to an adjacent position ion, and the other by the "free" electrons which pass between atoms which already have one valence electron.[9] The two processes are, of course, not altogether distinct. Both Slater and Bloch[10] have also considered the influence of the electron spin in its relation to ferromagnetism.

Recent developments[11] in this part of the theory have been principally concerned with more detailed studies of the motion of the electrons in the lattice using various modifications of Bloch's method. Careful study of the mathematical technique for handling this problem is a desideratum. It may perhaps be truly said that the new quantum mechanical theory of metals has in the main made progress through the power of its mathematical tools rather than by means of any really new physical ideas.

In this note we have, naturally, mentioned only salient points in the developments of the theory; reference must be made to the original literature for the details.

[6] F. Bloch, Zeits. f. Physik **52,** 555 (1928).

[7] J. Slater, Phys. Rev. **35,** 509 (1930).

[8] R. de L. Kronig, Proc. Roy. Soc. **A124,** 409 (1929).

[9] cf. E. H. Hall, Phys. Rev. **28,** 392 (1926).

[10] F. Bloch, "Uber die Wechselwirkung der Metallelektronen," Leipziger Vortrage, 1930. S. Hirzel. Leipzig.

[11] P. Morse, Phys. Rev. **35,** 1310 (1930); L. Brillouin, Jour. de Physique (7) **1,** 377 (1930).